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A Comparison between Optical Properties

Measured in the Field and the Laboratory,

and the Development of an Optical Model

A thesis submitted to the School of Ocean Sciences, University of Wales, Bangor, for the degree of Doctor of Philosophy

August 1997

SUMMARY

This thesis investigates the consistency of optical properties measured in situ and in the laboratory in order to construct a predictive optical model.

Fieldwork was undertaken at several sites which represented different aquatic environments, from clear ocean waters to dynamic estuarine systems. At each, diffuse attenuation and irradiance reflectance measurements were taken. Water samples were also collected for the determination of constituent concentrations and further optical analysis. Spectrophotometric measurements of sample absorption were taken in the laboratory, both from solutions in glass cells and particles on filters, with a comparison of different correction techniques.

Regression analysis was then used to calculate the specific absorption of different constituents and compare these with derived values from the in situ measurements. The derived specific absorption curve for phytoplankton was in close agreement with that presented in Gallegos et al (1990), while the exponential curve for yellow substance absorption agreed with Tassan (1988). Having derived these specific absorption curves with similar values to those found in the literature, the curve for mineral suspended particles was established as an exponential curve which decayed with wavelength to a constant value in the red. The use of different pathlength amplification factors with the laboratory spectra was used in comparison with the field measurements. A new correction equation was developed for mineral particles which resulted in closer agreement between the laboratory and in situ measurements than factors found in the literature.

The relationships between the constituent concentrations and the inherent optical properties can be changed to suit the particular environment if the precise characteristics (such as the dominant phytoplankton absorption spectrum or the size and refractive index of the sediment) are known. This enables the model to be used in a wider context for future studies.

Using these specific curves as a basis, an optical model was written. This model predicts absorption and scattering from the constituent concentrations and then calculates the resultant diffuse attenuation and reflectance across the spectrum and for PAR. This was found to work well for absorption and diffuse attenuation.

The greatest limitation to the model was the uncertainty in quantifying scatter, particularly in sediment laden waters where scatter will dominate the optical signal. The inability to include particle distribution and incorporate the precise particle characteristics which determine scatter led to a large error in the predictions which was then compounded in the reflectance values.

An inversion technique which assumed specific absorption values for each constituent at different wavelengths was then employed to write another model which derives the constituent concentrations from reflectance and diffuse attenuation values. This second model worked well for predicting mineral solid concentrations from an independent survey undertaken in the Menai Strait, but did not extend to other constituents.

It is concluded that for accurate predictive optical models a high degree of local knowledge of particle characteristics is necessary.

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 $\mathcal{A}=\{0,1,2,3\}$

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Many things have helped with the building of this thesis, particularly the patience from family and friends.

The most important thankyou is to my supervisor, Dave Bowers, who has cheerfully seen me through all sorts of dilemmas over the last few years and drawn me back to the issue in hand.

Contract Contract Contract

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1. INTRODUCTION

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People have always wanted to exploit the resources of the ocean and have therefore wanted effective methods for quantifying the various constituents present. Humans rely greatly on sight, and therefore light, everyday - the use of optical measurements to investigate underwater conditions is an extension of this. It is obvious that when water contains may particles the appearance is different to that of a pure water body

so the next step is to explain this change and relate the differences to concentrations. As colour, to the human eye, is highly subjective (Smith *et al*, 1995a & b), early methods developed knowledge of the loss of light overall, not the variation with wavelength. The broad band of visible electromagnetic radiation (400-700 nm) is known as Photosynthetically Active Radiation (PAR).

The first widely used tool for measuring light attenuation was the Secchi disk, studied and developed by Angelo Secchi in 1886, who discovered that the depth of disappearance was inversely proportional to the amount of organic and inorganic matter along the path of sight (Preisendorfer, 1986a). Although this disk bears the name of Secchi, it was used many years earlier. The first reported oceanographic cruise where optical measurements were taken was in 1817 (Hojerslev, 1994). This was the Rurik Circumnavigational Cruise led by Otto van Kotzebue who used a piece of red cloth lowered on a line to estimate the depth of light penetration. He later refined this method, using a white disk for measurements in the Pacific Ocean. This disk is still widely used today in conjunction with more sophisticated instruments and remains the easiest way to gauge the attenuation of light.

The progression of optical techniques has since relied on technical innovation. The first non-subjective measurements were taken using photographic equipment underwater. The initial study was by Fol and Sarasin in 1885 (Jerlov, 1968) where

they lowered photographic plates in the Mediterranean to a depth of several hundred metres (Hojerslev, 1994).

In 1890, Forel developed the colour scale (Austin, 1991) which was based on

 $\overline{1}$

comparing vials of different coloured mixtures of copper sulphate and potassium chromate (from blue to yellow) with the colour of the submerged white disk. Similar techniques are still used today as an immediate gauge of the water colour, notably the development of colour cards viewed just beneath the water surface (e.g. Davies-Colley et al, 1988; Davies-Colley & Close, 1990).

Also in 1890, theoretical optics was starting to develop with the paper by Ludwig

Valentin Lorenz investigating optical physics. However, this was published in Danish and it was not until 1915 that it was translated into French and became more widely appreciated (Hojerslev, 1994).

During the 1920s and 1930s extensive work was done with photoelectric cells by people such as Shelford and Gail (Jerlov, 1968) which led to advances in radiance and irradiance meters including Clarke in 1933 and Pettersson & Landberg in 1934. For greater detail, overviews of this development are given in Jerlov (1974) and Hojerslev (1994).

The first beam transmissometer was devised by Pettersson in 1934 (Jerlov, 1968), with

Kalle publishing important work on particle scattering in 1939. Kalle's work provided the basic parameters needed for particle distribution meters, which were subsequently developed and are still used today.

At the same time, the theoretical analysis of the light field was progressing through a series of papers by Shuleikin (1923 and 1933), and Gershun (1936 and 1939 - see Jerlov 1968 for details of these), in which he define the 'new' photometric concept of scalar irradiance. Another important paper was published in 1939 by Le Grand (see Jerlov, 1974), analysing the methods used in underwater optics and deducing the fundamental laws.

Since then, observational techniques have improved with the development of the photomultiplier tube in the 1950s and the use of lasers.

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On a different scale, remote sensing has broadened the spatial limitation of optics. The realisation that optical remote sensing could be useful occurred when photographs were taken from Sputnik on the Gemini and Apollo Earth orbital missions. These showed that different water masses could be distinguished. Following these photographs, airborne spectroradiometers were successfully used to differentiate water masses from their optical signal (Clarke *et al*, 1970 from Austin, 1991).

In 1978, the first satellite able to measure colour was launched the Coastal Zone Color Scanner (CZCS) - which operated for 8 years and led to the development of algorithms to derive constituent concentrations. Chlorophyll algorithms were particularly of interest to develop maps for global phytoplankton distributions and primary productivity.

More sophisticated colour satellites are now in orbit, or planned, to extend these optical classifications and derive concentrations with more accuracy. Much work has therefore been done on deriving constituent concentrations from optical properties with mixed success and often limited to the area of study.

The relationships between the inherent and apparent optical properties with the constituent concentrations are complex and all affect the observed water colour (Fig. 1). Thus, for any study concerning water colour, all three factors and their interactions must be considered. There has been a variety of models developed to help understand the links between the different properties (Appendix I), but there is more to be learned about the relationships, particularly for coastal water, and sediment laden areas.

The aim of this thesis is to establish observed relationships between certain optical properties and the constituent concentrations, concentrating on locations where mineral

suspensoids dominate the optical signal. The information gained from these observations will then be applied within a predictive model. The chapters therefore progress from field measurements through to the development of an ocean colour model. There is an introduction to the various optical properties, followed by a

description of the instruments used to measure them. The different sites and conditions are described to show the range of locations and the nature of the measurements at each site. This is followed by the methods and results for the field and then the laboratory measurements. The *in situ* and laboratory results are then compared to test their consistency, before being incorporated into a model which predicts absorption, scattering, beam attenuation, diffuse attenuation and reflectance from the constituent concentrations. Finally, an inverse model is developed to derive

concentrations from the optical properties.

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2. OPTICAL BACKGROUND

The definitions of basic optical properties which are discussed later in this thesis are given in this chapter. Definitions of further properties, to give a wider context, are presented in Appendix II.

The optical properties of a water mass are determined by the structure of the light

field and the nature of the substances within it. Properties which, by definition, are controlled by the light field, and are only indirectly affected by the substances, are known as apparent optical properties, such as diffuse attenuation and reflectance. However, some characteristics are solely governed by the constituents so that any variation is directly caused by a change in the concentrations. These are known as inherent optical properties, and include absorption, scattering, beam attenuation and the volume scattering function.

In order to use colour models for predictive purposes, or for monitoring concentrations, the relationships between the constituents and the inherent optical properties must be understood. This chapter describes the light field (§2.1), the apparent optical properties (§2.2), the inherent optical properties (§2.3) and then examines further relationships which have been described between various optical characteristics (§2.4).

2.1 LIGHT FIELD

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2.1.1 Radiance and Irradiance

The light field is usually described through radiance and irradiance. Radiance is defined as "the radiant flux per unit solid angle per unit projected area of a surface":

whilst irradiance is defined as "the radiant flux incident on an infinitesimal element

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of surface containing the point under consideration, divided by the area of that element" (Jerlov, 1968):

$$
E = \frac{d\Phi}{dA}
$$

and so describes the light from a hemi-spherical rather than a point source.

2.2 APPARENT OPTICAL PROPERTIES

2.2.1 Diffuse Attenuation

At any particular wavelength, the decrease in irradiance is described:

so that diffuse attenuation K is defined as "the vertical gradient of the logarithm of the quantity" (either radiance or irradiance):

$$
E(z) = E_0 e^{-Kz}
$$
 eqn. 2.1

where E is irradiance, E_0 is the irradiance immediately below the surface,

 K is the diffuse attenuation and z is depth

$$
K_x = -\frac{1}{E_x} \frac{dE_x}{dz}
$$

where the subscript x represents d or u for downward or upward

The net downward attenuation K_E is therefore defined:

$$
K_{B} = -\frac{1}{E_{d} - E_{v}} \frac{d(E_{d} - E_{v})}{dz}
$$

PAR attenuation is more rapid as the different wavelengths decrease at different rates, resulting in a steeper decrease near the surface. Most of the work in this thesis considers diffuse attenuation at discrete wavelengths, so that the exponential

The light field can be described in terms of the optical depth ζ , which is a gauge of the level of light compared with the surface. ζ is defined:

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N

$\zeta = K_d z$

Optical depths of 2.3 and 4.6 are particularly useful for phytoplankton studies, as these correspond to the mid-point and lower limit of the euphotic zone, where irradiance has decreased to 10% and 1% of the surface value (Kirk, 1994).

2.2.2 Reflectance

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Reflectance R is the ratio between upwelling and downwelling irradiance:

$$
R(\lambda) = \frac{E_{\nu}(\lambda)}{E_{d}(\lambda)}
$$

where λ is wavelength

although it is sometimes used as the equivalent ratio for radiance.

2.3 INHERENT PROPERTIES

where Φ_{\bullet} is the radiant flux lost from the beam by absorption, and Φ_{\bullet} is the incident flux

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When electromagnetic radiation hits a particle the electric field of the incident radiation causes the particle to change its energy level. The excited charges may then change the form of the energy (e.g. by converting it to heat) - absorption (Bohran $&$ Huffman, 1980), or reradiate energy - scattering.

2.3.1 Absorption

The absorption coefficient (a) is defined as the absorptance $(A - \text{see Appendix II})$ of an infinitesimally thin layer of the medium normal to the beam, divided by the thickness (Δr) of the layer

$$
a = -\frac{\Delta \Phi_{s}}{\Phi_{o}} / \Delta r
$$

The absorption coefficients of the different constituents are additive, so that the total absorption of sea water is:

$$
a = a_w + a_y + a_p
$$
 eqn. 2.2
a is the absorption coefficient for seawater, a_w is pure water, a_y is yellow
substance and a_p is particles

The characteristic shape of absorption curves between 400 and 700 nm for each component is shown in Fig. 2.1. Pure water has a defined absorption spectrum which increases with wavelength, tabulated by Smith & Baker (1981). Yellow substance (or Gelbstoff) absorption decreases exponentially from blue to red (Tassan, 1994):

$$
a_y(\lambda) = a(440) \exp[-0.014 (\lambda - 440)]
$$

where λ is wavelength in nm

Although Tassan uses an exponent of -0.014, values have been observed between -0.013 and -0.016 (Howard-Williams & Vincent, 1985 in Davies-Colley, 1992). Carder et al (1989) noted that a lower exponent indicates a higher contribution from the humic acids relative to the fulvic acids. This was also implied by Blough *et al* (1993) who noted that the exponential slope changed with salinity. Carder et al

and stage of development (e.g. Morel & Bricaud, 1981; Hoepffner & Sathyendranath, 1992; Babin et al, 1993; Moritorena & Guiliocheau, 1996; Sathyendranath et al, 1996) a single characteristic equation is difficult. However, chlorophyll-a is the dominant pigment in most phytoplankton, and is therefore considered representative.

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(1989) also found a change in the slope between the ultraviolet-blue range and the longer visible wavelengths.

Zooplankton can cause short term fluctuations in the observed optical signal (Austin 1970), but the biomass is less than 10 % that of phytoplankton (Bukata et al, 1981), and is therefore not considered to be a significant contributor to total absorption. Similarly, bacteria are not included in eqn. 2.2 as they do not make a significant contribution to absorption, although they have been studied for their scattering effect (Ulloa et al, 1992). Thus, the organic particles are considered to consist of phytoplankton and its detritus only. As the absorption spectrum varies with species This pigment has a double-peaked absorption curve, with a minimum in the green; the exact position of the peaks and the magnitude are altered slightly with the addition of extra pigments and detrital material. The specific absorption curve *(i.e.* the absorption due to one unit concentration) is multiplied by the concentration to determine the contribution of pigment to overall absorption.

Inorganic particle absorption is less well described in the literature. Kirk (1985) suggested that inorganic particles are pure scatterers and that absorption occurs due to organic material adsorbed on the surface (Bader *et al*, 1960; Davies-Colley, 1983). This conforms to the negative exponential curves which have been used for mineral particles (Gallegos *et al*, 1990). However, other factors have an influence on the absorption, and the exact shape and magnitude of the absorption curve is highly variable being dependent on the surface texture and hardness of the mineral constituents as well (Pak *et al*, 1970; Han & Rundquist, 1994 & 1996).

The theoretical link between irradiance and absorption is described (Voss, 1989):

$$
aE_0 = - \operatorname{div} E
$$

where E_0 is total scalar irradiance and E is net irradiance

As irradiance is assumed constant horizontally, this simplifies to:

$$
a = \frac{1}{E_0} \frac{dE}{dz}
$$

The average cosine μ is defined:

<u>ሃ</u>

the ratio of net to scalar irradiance

So that,

$$
a = -\frac{\mu(z)}{E_0(z)} \frac{dE_0(z)}{dz} - \frac{d\mu(z)}{dz}
$$

Alternatively, this can be written (Jerlov, 1976 in Setiapermana, 1990):

$$
a = \mu K_E
$$

where K_E is the difference in net irradiance between two depths considered

When measuring absorption by scanning filters in the laboratory, a pathlength amplification factor (β) is necessary, and is applied before the conversion to the

Direct measurement of absorption is difficult, as scattering is often included in any measurements. However, both laboratory and in situ instruments are being developed (e.g. Fry & Kattawar, 1988; Fry et al, 1992) which are based on an integrating sphere to minimize scattering effects. An integrating sphere has a totally reflective internal surface which redirects the light to a single point at which there is a sensor. Thus, all scattered light will eventually be recorded by the measuring sensor, so that any loss must be due to absorption.

absorption coefficient. This compensates for the effect of multiple scattering on the filter. β is defined as the ratio between the optical pathlength and the geometrical pathlength. To correct for β in phytoplankton cultures, Cleveland & Weidemann (1993) developed the conversion:

 $a(\lambda) = 0.378 A(\lambda) + 0.523 [A(\lambda)]^2$ where $a(\lambda)$ is the absorption coefficent, $A(\lambda)$ is the absorbance, or optical density, and λ is wavelength

The effect of this with increasing absorbance is shown in Fig. 2.2. A similar algorithm was developed in 1992, by Hoepffner and Sathyendranath:

$$
a(\lambda) = 0.31 A(\lambda) + 0.57 [A(\lambda)]^2
$$

Both of these corrections were based on measurements of phytoplankton cultures with

 $A(\lambda)$ < 0.4 and therefore are not ideal for the range of particle absorption studied in the Menai Strait. A more general correction, suitable for high absorbances, is $\beta = 2$ (Bricaud, pers. comm.); this assumes the multiple scattering is independent of wavelength. Alternatively, Balch & Kilpatrick (1992) inversely related β to the optical density.

There are three mechanisms of scatter by a particle (Williams, 1970): i) energy is reflected; ii) energy is refracted or diffracted; iii) energy is absorbed and then reradiated in a different direction but at the same wavelength (electromagnetic scatter). The first two processes are only relevant to particles which have a radius greater than 10 λ (*i.e.* 4-7 μ m); the third is therefore the dominant process in the ocean, as most scattering is due to particles with radius less than $1 \mu m$ (Kullenberg, 1953; Beardsley

2.3.2 Scattering

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Scattering is harder to quantify. Total scatter can be estimated by using instruments such as a nephelometer (Ganf et al, 1989), or an absorbance-scatterance meter (Bricaud et al, 1995), but is usually derived from other measurements or determined theoretically.

different angle to the incident light. This angle is dependent on the properties of the new medium, in particular the speed of light. The ratio between the incident and refracted angles is determined by the refractive index n , given by Snell's law:

et al, 1970; Stramski & Kiefer, 1991). In pure water, molecular (or Rayleigh) scattering is most important, involving particles less than or equal in diameter to the wavelength of light. The amount of scatter across the spectrum follows λ^{-4} and leads to Raman emission as light is reradiated at a lower energy level and, therefore, a longer wavelength. Most sea water contains particles with diameter $> \lambda$ (Kullenberg, 1968), particularly Case 2 waters. As this thesis mainly considers coastal or inland waters, Rayleigh scattering is inappropriate and therefore is not included in the calculations.

When light crosses an interface or hits a particle, the refracted energy continues at a

$$
n = \frac{\sin i}{\sin j}
$$

where i is the angle of incidence and j is the angle of refraction

Electromagnetic scattering was described by Mie, in 1908, assuming homogeneous, spherical particles. This is not an exact representation of the natural environment but a good approximation (Jerlov, 1968). The theory determines scattering with an efficiency factor K_f :

Sea water has a refractive index of 4/3 relative to air.

$$
K_f = \frac{4 I_T}{\pi D^2}
$$

where I_T is the total scattered radiation and D is the diameter of the particles

As the particle radius increases, K_f oscillates in value until it becomes steady at approximately 2. This occurs at a radius of $3-5 \mu m$ (Thompson *et al*, 1979).

The scattering coefficient is related to the efficiency factor, the number of particles

per unit volume (N), and the diameter (D) of the particles (assuming a monodisperse system):

$$
b = \frac{K_f N \pi D^2}{4}
$$

For polydisperse systems (which include particles of various sizes) this becomes:

$$
b = \frac{\pi}{4} \sum_{i=1}^{n} K_{fi} N_{i} D_{i}^{2}
$$

Thus, if there are only two predominant particle sizes, the overall scatter is calculated

as the sum of the two separate scattering distributions, not the scatter calculated for an average size (Zaneveld et al, 1974).

The efficiency factor employed here is suitable for particles which are pure scatterers;

when particles also absorb, an imaginary term must be included in the refractive index:

$$
m=n-im'
$$

where $n' = a\lambda/4\pi$ and a is the absorption coefficient

Consequently, the efficiency factor is lowered resulting in less overall scatter (Voss, 1992). This is confirmed with observations by Bricaud & Morel (1986). An average value of 1.15 for the real term can be used for mineral suspensoids, such as clay and

silt (Williams, 1970), whereas $n < 1.05$ is appropriate for phytoplankton (Jonasz & Prandke, 1986). This illustrates the difference between mineral and organic particles (which absorb more) even when the imaginary term is omitted.

ranges from 0.0001 to 0.002 (Morel & Bricaud, 1981b). This shows that the contribution by living algae to backscatter is relatively small (Ahn *et al*, 1992).

The volume scattering function β_v , (O) is a more accurate description of the light distribution, quantifying the proportion of energy scattered in all directions:

where $dI(\theta)$ is the intensity in the direction of the incident beam and dV is the volume element irradiated

The proportion of light which is scattered backwards is variable. Kirk (1981a) assumed a value of 0.019 in turbid water, although Gallie & Murtha (1992) found a log relationship with suspended mineral concentration. The amount of backscatter can be related to absorption, as both the backscatter ratio and the scattering coefficient are altered by changes in a (Morel and Prieur, 1981). Thus, although a backscatter ratio of 0.019 is assumed for inorganic particles (Kirk 1981a), the value for phytoplankton

2.3.3 Volume Scattering Function

$$
\beta_{\nu}(\theta) = \frac{dI(\theta)}{EdV}
$$

Petzold (1977) measured the volume scattering function in different water masses and

found that although it varied in magnitude with the nature of the water, it remained

approximately the same shape, with 18-28% of the radiation scattered between 0° and

1.0°, 50% within 5° (Di Toro, 1978), and up to 75% scattered within 10°. This tendency towards forward scattering in the natural environment, is due to the presence of particles (Tyler, 1961), as molecular scattering is uniform over all angles. Thus, forward scatter becomes more pronounced in turbid water (Kullenberg, 1974). Even in very clear water a predominance towards forward scattering indicates the presence of small particles (Ochakovsky, 1966). Forward scattering is independent of wavelength but as the angle increases, and molecular scattering becomes relatively more important, the wavelength dependence increases, becoming greater at shorter wavelengths (Kullenberg, 1953; 1968; Kirk & Oliver, 1995). The difference in scattering between mineral and organic particles is also apparent in the volume scattering function. This difference enabled Pak et al (1970) to determine the type of particles in the water column from the vector diagram of scattering. They identified predominantly biological particles at the surface through to geological at greater depths. However, below a certain depth, $\beta_v(\theta)$ is less useful as the light becomes totally diffuse (Preisendorfer, 1959).

Beam attenuation (c) is the total amount of energy "lost" from a direct path through the water, and is defined as the sum of absorption and scattering. The beam attenuation coefficient is always greater than the diffuse attenuation, and is the equivalent to the radiant flux of K to irradiance:

Although the volume scattering funcction is an important parameter for describing the light field it was not possible to measure this in the field. It has therefore been

neglected within the analysis and the variation assumed negligable.

2.3.4 Beam Attenuation

 \sim \sim

$$
\Phi = \Phi_0 e^{-ct}
$$

where Φ is the radiant flux, Φ_0 is the initial radiant flux and r is the length

As this is the easiest inherent property to measure, using a transmissometer, the relationship between c and suspended solids has been investigated in several studies

(e.g. Ivanoff et al, 1961; Spinrad et al, 1983; Trowbridge et al, 1994). It has been found that c is directly related to concentrations of particles of radius $\lt 100 \mu m$ (Campbell & Spinrad, 1987).

As discussed in §2.3.1 and §2.3.2, the composition of the particulate matter greatly influences the relative effectiveness of scatter and absorption, and consequently, the beam attenuation. With more particles in the water, the attenuation is higher, while a relative increase in scattering produces an increase in reflectance. It is therefore possible to estimate a depth profile of particle concentrations from the attenuation profile in clear ocean water. On this basis, Jerlov (1968) classified sea water into different types, identified by the attenuation curve. Three of these were for open ocean and nine for coastal regions, the latter type having much higher attenuation values and more complex interactions (Fig. 2.3). Any site could fit a basic profile with a similar magnitude, although Jerlov expected variation within each type at different locations. The aim was to extend these classifications to the properties within the water, and ultimately, the productivity so that nutrient-rich areas could be identified.

The Secchi depth z_{SD} is dependent upon both apparent and inherent optical properties but shall be explained here, as it mainly depends on the constituent concentrations. This depth is that at which the white Secchi disk can no longer be seen when lowered into the water. It is measured by markers on the rope and indicates the overall clarity. Consequently, the recorded depth is subjective, and can change with the viewer; it is also dependent on the reflectance and surface area of the disk (Edmondsen, 1980), the amount of shading and the state of the water surface (Tyler, 1968). However, it remains a workable estimate of clarity.

Given these complications, it has been suggested that z_{SD} should only be used as an indication of clarity, or contrast, and not as a quantifiable parameter (Preisendorfer, 1986b).

2.3.5 Secchi Depth

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2.4 RELATIONSHIPS BETWEEN PROPERTIES

2.4.1 Radiance and Irradiance

Both the Satlantic and the PRR600 measure downwelling irradiance E_d and upwelling radiance L_{μ} . These measurements are designed to correspond to satellite observations, but cannot be used to directly calculate subsurface irradiance reflectance. It is therefore necessary to know the relationship between radiance and irradiance. If a

Lambertian reflector is assumed, then:

$$
E_{v} = \pi L_{v}
$$

 K_d and R can be related to downward backscatter b_{bd} by defining another optical property $\kappa(z)$, which is "the average vertical attenuation coefficient in upward travel from the first point of upward scattering of all upwelling photons at a given depth" (Kirk, 1994). The relationship can then be described:

However, water does not usually act as a Lambertian reflector as radiance is not equal at all angles. Kirk (1994) used a Monte Carlo model to estimate the ratio E_{μ}/L_{μ} , with a solar altitude of 45°, and found this to be approximately 5. However, this value does not appear to be constant (Smith, pers. comm.), as the ratio varies with local conditions, so the use of one conversion factor is not appropriate.

2.4.2 Apparent and Inherent Optical Properties

$$
R(z) \approx \frac{b_{bd}(z)}{K_d(z) + \kappa(z)}
$$

Monte Carlo models have shown that κ is approximately proportional to K_d (Kirk,

1994) at the mid point of the euphotic zone (z_m) :

$$
\kappa(z) = 2.5 K_d(z)
$$

Through the use of radiative transfer theory (Appendix II) a relationship can also be

established between K_d and a. In 1936, Gershun (from Kirk, 1994) derived the relationship:

$$
\frac{d\vec{E}}{dz} = -cE_0 + bE_0 = -aE_0
$$

where \vec{E} is net downward irradiance

which describes the downward diffuse attenuation as the sum of the downward absorption and backscatter *(i.e.* the loss from the light field), minus the product of

$$
a = K_E \frac{\vec{E}}{E_0}
$$

$$
a = K_E \overline{\mu}
$$

Preisendorfer (1961, from Kirk 1994) derived a relationship with the diffuse absorption and scattering coefficients:

$$
K_{d}(z) = a_{d}(z) + b_{bd}(z) - b_{ba}(z)R(z)
$$

upward backscatter and reflectance (which add a component to the level of light and thus decrease the attenuation).

A simplified version of the radiative transfer theory can be used to show that $R(0)$, the reflectance at the surface, is proportional to $b_b/(a+b_b)$, but as b_b is much lower than a is approximately proportional to b_b/a , which leads to (e.g. Morel & Prieur, 1981):

$$
R(\lambda) = 0.33 \frac{b_b(\lambda)}{a(\lambda)}
$$
 eqn. 2.3

However, this is only an approximation as the constant of proportionality (0.33) is

dependent on the solar altitude (Kirk, 1994). Kirk (1985) incorporated the solar

variation by changing this constant as μ_0 (the average cosine):

$$
R = [0.975 - 0.629 \mu_0] \frac{b_b}{a}
$$
 eqn. 2.4

If the value of 0.85 is assumed for μ_0 the constant becomes 0.44.

Through the use of Monte Carlo models, Kirk (1994) has shown that for K_d at the

mid-point of the euphotic zone:

$$
K_d(z_m) = (a^2 + Gab)^{1/2} \qquad \text{eqn. 2.5}
$$

The above equations can be rearranged to calculate a and b . If the backscatter ratio is assumed to be 0.019 (Kirk, 1994), then

For water with the same volume scattering function as San Diego Harbour, Kirk (1994) has calculated that G=0.256. For the average K_d through the whole euphotic zone G=0.231. G determines the proportion of the diffuse attenuation which is 'lost' through scattering. In turbid water, the value of G will be lower as forward scatter will dominate and be backscattered into the path, whereas in clear water, the energy is lost with uniform scatter in all directions.

$$
\frac{b}{a} = \frac{R}{(0.33, 0.019)}
$$

while

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$$
\frac{K_d}{a} = \left[1 + G\frac{b}{a}\right]^{1/2}
$$

 $a = \frac{(K_d / a)}{K_d}$

Both reflectance equations were used in the derivation of a and b , as although 0.33 is a general value which does not include the effect of solar altitude, the value of 0.85 for μ_0 , based on the optical properties of San Diego Bay (Petzold, 1977), is also unrealistic.

The Secchi depth can be related to both diffuse and beam attenuation. In general, it is not directly related to K_d , although empirical studies have suggested that at 505 nm

 $K_d = 3.35/z_{SD}$ (Man'kovskiy, 1978) and for PAR, $K_d = 1.44/z_{SD}$ (Holmes, 1970). Tyler (1968) deduced that $(c+K_d) = 8.69/z_{SD}$, while observations by Holmes (1970) suggest $(c+K_d)$ = 9.42/ z_{SD} . Davies-Colley and Close (1990) simplified the interpretation by taking horizontal clarity measurements with a black disc so that only c is measured. Using this method, Davies-Colley and Smith (1995) measured almost maximum theoretical clarity in a New Zealand freshwater spring - 63 m visibility. This technique also enables measurements in shallow lakes where depth is only one or two attenuation depths.

2.4.3 Apparent Optical Properties and Constituents Controlled studies, which have increased the level of suspended sediment concentration, have found a non-linear relationship with reflectance (Curran & Novo, 1988), with the correlation improving at higher wavelengths (Han & Rundquist, 1994a). The gradient of the correlation is lower with finer material (Han & Rundquist, 1996). In general, the peak reflectance moves towards higher wavelengths with increased concentration (Tassan, 1988; Gitelson, 1992; Han & Rundquist, 1994b).

Both Novo et al (1989) and Bhargava & Mariam (1990) have noted that the reflectance spectrum changed with sediment type as well as concentration. Consequently, the reflectance has been used to identify sediment (Hunt, 1977). The higher the organic content in the sediment the lower the general level of reflectance (Bhargava & Mariam, 1990). In the laboratory, reflectance is most easily measured when the sediment is pulverized (Balsam & Deaton, 1991), with the spectra being used to distinguish different sediments (e.g. Hunt & Salisbury, 1976; Hunt & Ashley, 1979) or even different minerals and the water content (Gaffey, 1985; Deaton & Balsam, 1991; Balsam & Wolhart, 1993). However, although these investigations are used for bed analysis they have not been extended to *in situ* measurement where laboratory procedures are not possible.

In many of these reflectance studies, the derivative of the spectrum is used to highlight the changes in the curve (Goodin *et al*, 1993). This technique has also been used for phytoplankton analysis to distinguish between pigments (Sathyendranath et al, 1994).

As attenuation has been used to classify different marine water, so reflectance has been used to classify lakes into 5 categories (Vertucci & Likens, 1989), showing the change from clear water through increasing pigment and yellow substance concentrations (Fig. 2.4).

When observations are taken in water which is not deep enough to eliminate bottom effects, the reflectance value is a function of bottom albedo and depth of the water (Maritorena et al, 1994). This is useful for sea bed studies in shallow water as the effects will depend on the nature of the bed (Estep, 1994), but to investigate the constituents in the water column itself deeper water is essential.

In previous studies, yellow substance has been related to salinity; Kalle (1966) found a strong inverse relationship, while Davies-Colley (1992) did not find any link. It is assumed that the freshwater contains a higher concentration of humic acids, so that as the fresh water is diluted, becoming more saline, so the yellow substance concentration decreases. This was used successfully to identify the mixing process with water from the Baltic Sea and from clearer oceanic water (Jerlov, 1968).

2.5 REMOTE SENSING

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Airborne or satellite sensors can be used to monitor water quality (McNeil *et al*, 1976; Thomas, 1981), and identify different water masses and events (Topliss *et al*, 1991). Airborne sensors are the most effective method of monitoring, with spectroradiometers used to differentiate different water bodies since Clarke et al's work in 1970 (Austin,

1991). However, this method is expensive and is subject to a greater water surface effect than satellites (van Stokkom *et al*, 1993). There are several satellites carrying visible light sensors which have recently been launched or are planned, with the successful launch of ADEOS in August 1996, and the prospective launches of SeaWiFS and a similar European satellite. These give greater spatial and temporal coverage of the ocean than airborne techniques. Previously, the only sensor designed for ocean colour measurements was the Coastal Zone Color Scanner (CZCS) which

operated between 1978 and 1986. The data from this have subsequently been studied

in great detail in order to develop workable monitoring algorithms to identify and quantify phytoplankton. The LANDSAT satellites have two visible band sensors - the Thematic Mapper and the Multi-Spectral Scanner - which can be used to observe sediment (indicated by a high overall reflectance signal) and distinguish pollutants (Munday & Alfoldi, 1979; Sydor, 1980; Schiebe et al, 1992).

Predominantly, the work on the CZCS data considers ratios of the upwelling light, and how these are related to chlorophyll concentrations from ground truth data. The sensor had four bands of 20 nm bandwidth centred on 443 nm, 520 nm, 550 nm and 670 nm; most ratios involve blue to green comparisons (Gordon et al, 1980; Morel, 1980; Neuymin et al, 1982; Smith & Baker, 1982; Parslow, 1991; Mittenzwey et al, 1992) while some used green to red or a combination of ratios (Bukata et al, 1981b). Alternatively, the difference between wavebands may be used (Giannini, 1981). Viollier & Sturm (1984) specified that the constants used for the algorithms would change with phytoplankton type, and between the range of studies undertaken there is a great variation, as shown in Table 2.1. Other studies have quantified the effect of sediment on these ratios (Simpson & Brown, 1987; Brown & Simpson, 1990; Quibell, 1991). The depth of the euphotic zone has been shown to have an effect on the algorithms (Hojerslev, 1980 & 1981), while better agreement has been found when depth-averaged values of chlorophyll were used rather than just the surface value

(Anderson et al, 1981; Smith, 1981).

Other constituents have been shown to interfere with these algorithms, as Hochman et al (1994 & 1995) found that half the supposed chlorophyll signal was due to

dissolved organic matter. There are also algorithms to derive sediment concentrations, but these become less effective when organic concentrations exceed 1 mgl⁻¹ (Agnew, 1983), although once the sediment concentration is above 25 mgm^3 the chlorophyll signal is much weaker (Holyer, 1978).

A further limitation with satellite measurements is the necessity for good atmospheric algorithms prior to the interpretation of the ocean signal (Viollier et al, 1980; Sturm,

1981; Smith & Wilson, 1981).

$\log C = \log a + b \log (Rt) \rightarrow C = a Rt^{b}$					
Author	a		Rt		Comments
			Gordon <i>et</i> $\ 0.505 - 1.269 L_w 443/L_w 550$		Only applies for
al (1980)			\parallel 0.843 -3.975 L _w 520/L _w 550		$C < 0.6$ mgm ⁻³
Clark			0.766 -1.329 L_w 443/ L_w 550	0.908	Also used by Austin
					(1981) $\begin{bmatrix}\n0.700 & -1.222 & -w & -w & -w \\ 0.518 & -1.806 & L_w 443/L_w 520 & 0.874 & & \& \text{Petzold (1981)} \\ 1.694 & -4.449 & L_w 520/L_w 550 & 0.913 \\ 48.853 & -1.372 & L_w 520/L_w 670 & 0.876\n\end{bmatrix}$
					Smith & $\begin{bmatrix} 0.483 & -3.08 & L_w 443/L_w 520 & 0.882 &$ Only applies for Wilson $\begin{bmatrix} 0.783 & -2.12 & L_w 443/L_w 550 & 0.943 & 0.05 < C < 5.0 \text{ mm}^3 \end{bmatrix}$
(1981)	$\ 2.009 - 5.93 \ $		L_w 520/ L_w 670		
Sturm	0.5	-1.3	L_w 443/ L_w 550		After Gordon et al
(1981)					(1979) C<1 mgm ⁻³
	$\vert 0.8 \vert$	-4.0	L_w 520/ L_w 550		After Gordon (1980)
					$C>1$ mgm ⁻³
		-2.0	L_w 443/ L_w 550		After Morel & Prieur
					(1978)
		-2.7	L_w 443/ L_w 550		Average over all
Topliss et al $\left\ \begin{array}{c} 1.2 \\ 1.2 \\ (1991) \end{array} \right\ $ 2.9		-6.4	L_w 520/ L_w 550		concentrations

concentrations

Optical remote sensing is important to give a wide spatial coverage at low cost. Most work has tried to develop algorithms for extracting chlorophyll concentrations in Case 1 waters with the aim of estimating primary productivity. There has been less work with coastal waters where the chlorophyll signal is dominated by that from sediment and yellow substance.

The quantitative use of satellite images is dependent on the development of inverse

In order to compare the inherent and apparent properties it is necessary to derive the inherent optical properties of absorption and scattering from the apparent properties measured *in situ* using the equations in §2.4.2. This method rearranges the equations

calculated from observations and modelling of a turbid environment described by Kirk (1985). The derived values of the absorption coefficient can then be related to the absorption measured in the laboratory. Consequently, diffuse attenuation and reflectance need to be measured in the field. It is also useful to measure beam attenuation in the field so that scattering can be determined once the absorption coefficent is known. Beam attenuation was the only possible inherent property that could be measured in situ with the instrumentation available, but can give a direct field comparison between the inherent and apparent properties using $c=a+b$ with the derived a and b values and is therefore an important parameter. In total, observations were taken of K_d , R and c in the field (plus ambient light measurements), and a in the

laboratory, with a experimentation to determine the importance of b.

optical models, deriving the concentrations of phytoplankton, yellow substance and sediment from the upwelling radiance. However, other models which aim to understand the interactions between these constituents and how they effect the reflectance signal aid general interpretation of the images, and can lead to better inversion techniques in the longterm.

2.6 SUMMARY

Figure 2.1 Examples of specific absorption curves for
a) water

-
- a) water
b) yellow b) yellow substance
c) phytoplankton
-
- c) phytoplankton d) inorganic particles

 $\mathcal{L}^{\text{max}}_{\text{max}}$, where $\mathcal{L}^{\text{max}}_{\text{max}}$ $\sqrt{2}$, $\sqrt{2}$ $\mathbf{S}^{(n)}$ and $\mathbf{S}^{(n)}$ and the contract of $\mathcal{O}(\mathcal{O}(\log n))$. The $\mathcal{O}(\log n)$ $\label{eq:2.1} \mathcal{L}_{\mathcal{A}}(x) = \mathcal{L}_{\mathcal{A}}(x) \mathcal{L}_{\mathcal{A}}(x) = \mathcal{L}_{\mathcal{A}}(x) \mathcal{L}_{\mathcal{A}}(x)$ $\mathcal{L}^{\mathcal{L}}(\mathcal{F},\mathcal{S})$, and $\mathcal{L}^{\mathcal{L}}(\mathcal{F})$

 $\mathbf{X}^{(n)}$ and $\mathbf{X}^{(n)}$. In the $\mathbf{X}^{(n)}$ $\mathcal{L}(\mathcal{A})$. The set of $\mathcal{L}(\mathcal{A})$ $\mathcal{L}^{\mathcal{L}}$ and $\mathcal{L}^{\mathcal{L}}$ and $\mathcal{L}^{\mathcal{L}}$ and $\mathcal{L}^{\mathcal{L}}$ $\mathcal{L}(\mathcal{A})$ and $\mathcal{A}(\mathcal{A})$ $\mathcal{L}^{\text{max}}_{\text{max}}$. The $\mathcal{L}^{\text{max}}_{\text{max}}$ \mathbf{r} , and \mathbf{r} $\label{eq:2.1} \mathcal{L}_{\mathcal{A}}(x,y) = \mathcal{L}_{\mathcal{A}}(x,y) + \mathcal{L}_{\mathcal{A}}(x,y) + \mathcal{L}_{\mathcal{A}}(x,y) + \mathcal{L}_{\mathcal{A}}(x,y)$ $\mathcal{L}(\mathcal{$

 $\sim 10^{-11}$

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Figure 2.4 Reflectance curves used to classify lakes. Adapted from Vertucci & Likens (1989)

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 \mathbf{X} $\sim 10^{-11}$ \mathbf{K}

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3. INSTRUMENTATION

3.1 FIELD WORK

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Seven types of optical sensor were used over the different surveys, including two built by UCNW staff, and five commercially manufactured. To measure vertical attenuation and reflectance the upwelling and downwelling radiance or irradiance must be quantified at different depths. This can either be the absolute or the relative value,

- white disk of 30 cm diameter
- \cdots rope marked at 0.5 m for depth measurement

as the ratio is needed, not the exact quanta of energy present.

The UCNW instruments were passive sensors which measured relative irradiance at different wavebands, and could be oriented to measure either the upwelling or downwelling signal. Specifications of all instruments are given below:

Secchi Disk

- 7-Channel (Fig.. 3.1) IRM1
	- -5 visible channels, 1 UV and 1 unused
	- readings averaged over three seconds
	- sequential wavelength readings
	- 10 nm bandwidth, centred on 444 nm, 521 nm, 552 nm, 596 nm and 670 nm (response curves are shown in Appendix HI)
	- pressure sensor, accuracy to 0.1 m
	- instrument surrounded by a weighted, protective frame to maintain a vertical
	- orientation in the water, within which the sensor could be turned upside down
	- connected by a cable to a deck unit, which was computer driven to store data
	- surface cosine collector also connected to deck unit to monitor the ambient

light field

- relative calibration

This instrument measured the downwelling light at different depths, being kept at at each level for 20-30 seconds. It was then brought back to the surface and the sensor

inverted to measure upwelling light. A second 'profile' was then done keeping the sensor at each depth for the same amount of time again. This resulted in a time lag of several minutes between the start of the downwelling profile and the end of the upweling profile, although simultaneous surface readings were taken to monitor the changes in ambient light over this period.

4-Channel (Fig. 3.2) - CS2, CS3, CS4, CS23, CS24

- -4 visible channels
- 10 nm bandwidth, centred on 440 nm, 490 nm, 570 nm and 670 nm
- one sensor, CS24, fitted with a pressure sensor, accuracy ± 0.1 m
- internal logging
- relative calibration

The CS24 could be used to measure profiles in a similar manner to the IRM1, as a pressure sensor was fitted. However, the other sensors were used at fixed positions either near the bed looking upwards, when a tide gauge was available, or using floats \cdots on the surface looking downwards. These could be configured for different sampling intervals, from 30 seconds to 30 minutes dependent on the nature of the deployment.

The commercial instruments included a Satlantic, PRR-600, transmissometers, and a surface radiometer: Spectron SE590.

Satlantic

 \sim $-$

- designed to coincide with the SeaWiFS satellite channels
- one irradiance sensor, usually positioned to measure the downwelling signal:
	- 7 visible wavebands of 10 nrn bandwidth,

centred on 410 nm, 440 nm, 490 nm, 510 nm, 550 nm, 670 and 700 nm

- one radiance sensor, to measure the upwelling signal:

7 visible wavebands

centred on 410 nm, 440 nm, 490 nm, 510 nm, 550 nm, 685 and 700 nm

- pressure sensor
- internal logging
- weighted frame to maintain vertical orientation
- relative calibration

The sampling period could be set to 1 second which enabled profiles to be performed with a smooth lowering of the instrument. This produced more accurate measurements of the vertical attenuation. However, although there were upward and downward looking sensors the reflectance could not be directly calculated as the relationship between radiance and irradiance was unknown. Consequently, the

instrument was lowered smoothly through one profile, then brought to the surface and

inverted so that the sensors were in the opposite orientation, and a second profile was

taken. There was therefore always an error added to the calculation of reflectance

either by the conversion of radiance to irradiance or the time lag between profiles.

PRR-000 -

- designed to coincide with the SeaWiFS satellite channels
- one irradiance sensor, usually positioned to measure the downwelling signal:
	- 6 visible wavebands of 10 nm bandwidth,

centred on 410 nm, 440 nm, 490 nm, 510 nm, 550 nm and 665 nm

1 PAR band

- one radiance sensor, to measure the upwelling signal:
	- 7 visible wavebands
- centred on 410 nm, 440 nm, 490 nm, 510 nm, 550 nm, 665 and 685 nm
- pressure sensor
- temperature sensor
- cable connects the instrument to a computer which logs the data
- relative calibration

This instrument had similar limitations to the Satlantic, having a fast sample rate to

enable accurate profiles of radiance and irradiance to be taken, but necessitating the

inversion of the whole instrument to calculate reflectance.

Intercomparison of these instruments occurred in the Menai Pier Surveys. The colour sensors were compared in air after the first survey. Although the absolute readings were different, the ratios between the colour bands were the same and the variations with light level were consistent. It was hoped to compare the CS24, IRM1 and Satlantic in the August 1995 Survey but due to the malfunctionsing of the CS24 and the inability to download the Satlantic on two occasions this opportunity was not realised.

Profiling Transmissometer SBE 19 Seacat Profiler

- 10 nm band width, centred on 670 nm
- 20 cm pathlength
- attached to a CTD:

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conductivity, which is converted to salinity
```
temperature

pressure

Transmissometer

- 10 nm band width, centred on 670 nm
- 25 cm pathlength

Spectron SE590 -

- one cosine receiver for ambient light
- one spectral sensor with 15° field of view
- -2m beam to enable deployment out of shadow effects
- total range 368 nm to 1115 nm, measuring at 2 nm intervals within the visible spectrum
- wavelengths measured simultaneously, averaged over four readings
- both sensors attached to a manually controlled deck unit, data written to tape then transferred to ASCII format later

To confirm that the sensors were not drifting, the spectral sensor was directed at a

spectralite sheet after every fifth reading. If the reflectance signal was close to 100%

across the spectrum when compared with the cosine sensor, this verified that the

sensors were performing correctly.

3.2 LABORATORY

Instruments

The laboratory equipment required included spectrophotometers, a Turner fluorometer and balances. Due to problems with various instruments, three spectrophotometers and three balances were used between 1993 and 1996.

3.2.1 Spectrophotometers

1) Hewlett Packard Diode Array

used for Menai Strait Survey November 1993-June 1994, Conwy and Cwmystradllyn, summer 1995

2) SHINIADZU UV-1201 Scanning Spectrophotometer

used for all spectra taken until September 1995 (other than those mentioned above), and inorganic spectra November 1993-June 1994 20 W Halogen lamp

monochrometer: concave holographic grating

detector: silicon diode

```
wavelength accuracy \pm 1.0 nm
photogrammetric range: -0.3 \rightarrow 3.0 Abs units
accuracy \pm 0.005 Abs
repeatability \pm 0.002 Abs
```
3) SHIMADZU UV-1601 Scanning Spectrophotometer used for all spectra after September 1995, plus the inorganic spectra for Menai Pier Survey August 1995 also used to derive pigments from Cwmystradllyn, Conwy and the Clyde surveys during 1996

3.2.2 Turner Fluorometer

used to measure chlorophyll related pigments for all surveys except Vestfjorden, Cwmystradllyn, Conwy and Clyde Sea surveys in 1996

3.2.3 Balances

All balances were calibrated periodically by NAMAS accredited technicians. For consistency, the balance which was used to pre-weigh filters was used through all stages of the filtering process.

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Menai Pier Survey 1994 accuracy 10^{-5} g

1) METTLER INSTRUMENTE AG CH-8606

used for Menai Strait Survey, Cardigan Bay, Clyde Sea accuracy 10' g

2) OERTLING

3) OHA US ANALYTICAL Plus DB2

Vestfjorden, Menai Pier Survey 1995, Conwy, Cwmystradllyn accuracy 10-5 g

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Figure 3.2 UCNW Colour Sensor (CS)

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Figure 3.4 PRR-600 and Profiling Fluorometer

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4. FIELD SURVEYS

Surveys were undertaken in a range of water types to distinguish the different optical environments. Most of the data were collected in the Menai Strait, but other marine sites were included, plus estuarine and freshwater locations to provide a contrast. The various sites with the different instruments used are given in Table 4.1 chronologically, with details of the surveys then described below, while standard

methods for the field and laboratory measurements are given in chapter 5.

4.1 MENAI STRAIT SURVEY

The Menai Strait separates Anglesey from mainland northwest Wales. In this area, there is a series of northeast-southwest depressions where the drainage has exploited the weaker geology due o faults of Caledonian origin (Asghar, 1992). The Strait formed in such a valley whih was overdeepended during the last glacial maximum, and was finally flooded in the Flandian transgression: 6000-7000 BP (Embleton, 1964). The glacial histor of the region has resulted in a general stratigraphy of Upper Boulder Clay overlying meltwater sands and then Lower Boulder Clay, although the upper layer of this succession has subsequently been eroded within the Strait (Jones, 1978). The sources of sediment include run-off from the land, but mainly consist of sea floor deposits, *i.e.* boulder-clay from the Conwy Bay area, and sand/lag-gravel deposits from the Irish Sea.

Ten sites along the Menai Strait (Fig. 4.1) were visited every month from November 1993 to October 1994, with the exception of April and September. The positions (Table 4.2) were easily identifiable, out of the main current and covered a range of environmehtal conditions. These were chosen to give a contract of optical conditions due to the different surroundings as described in the comments.

the field

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Table 4.2 Description of sites along the Menai Strait

Throughout the Menai Strait the water is vertically well mixed, confirmed by the transmissometer profile in Fig. 4.2, indicating that surface water samples were representative of the upper 12 m of the water column. The readings were taken at various points in the spring-neap cycle (Fig. 4.3), dependent upon weather conditions.

The UCNW Irradiance meter (IRM1), used to measure K and R, was lowered from a small powered boat (the Sandpebbler). Water depth was measured with the boat's

sonar, while ambient light and Secchi depth readings were taken. Downwelling light was measured at approximately 3, 2, 1 and 0.5 m, while upwelling was measured at 1 and 0.5 m. These depths were adjusted according to the water clarity, profiling to a greater depth in clearer water. All sites were visited within a day, except for the November survey when 1-4 were visited on 17 November and 5-10 on the following day. In January and October deteriorating weather conditions prevented data collection at all sites, limiting data to sites 4-8, and 2-10 respectively. A total of 94 stations was taken over the year.

A bucket was lowered over the side to collect water samples, which were stored in

plastic bottles in black bags during the day until the boat returned to the laboratory in the late afternoon. 2.5 1 of water were collected at each site, 11 to be filtered for suspended particulate matter (SPM), and 3x250 ml for chlorophyll extraction and yellow substance measurement.

4.2 MENAI PIER SURVEY

In both 1994 and 1995, measurements were made for two weeks at the end of the floating Menai Bridge Pier. Daily samples were taken to determine constituent concentrations, while optical instruments were deployed. Different sensors were used for the two surveys, so they will be described separately.

4.2.1 July 1994

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The two week period, 11-25 July, covered a spring-neap-spring cycle, with water samples taken at noon each day. For one 24-hour period (21-22 July), hourly samples were taken to identify any semi-diurnal signal. In addition, seven Spectron measurements, and eight IRM1 profiles were made.

Three 4-channel colour sensors were used: CS2 was positioned on the roof of the Westbury Mount Building, and took one reading every 30 minutes - this was the overall reference to evaluate ambient changes. CS4 was attached to a low strut of the southern tower of the pier, 0.83 m beneath chart datum, measuring downwelling light. CS3 was deployed daily, between 08.00 and 17.30, to measure upwelling light at a depth of 0.5 m. A transmissometer was also attached to the pier, 2m below the platform.

measure the 'wet' spectrum, while all were scanned after drying and again after furnacing (refer to §5.2.4.). It was discovered that salt remained on the SPM filters,

During the first week the Spectron was used to measure the surface reflectance, and sub-surface reflectance by taking readings through a black pipe (to minimize the surface effect - see §5.1.2 for details). The IRM1 was deployed to identify changes in the radiance profile. These measurements were taken on 11-15,18-19 and 22 July, to establish independent reflectance and attenuation values.

Each day at noon, a tidal height reading and Secchi depth were taken. 51 of water

were collected and analysed in the laboratory. The concentrations of pigment and

SPM (3 replicates for each) were measured, with the filtrate used for yellow substance

absorption. One filter was immediately placed in the UV 1201 spectrophotometer to

enhancing the particle weights. The filters were therefore re-rinsed several weeks later, which increased the uncertainty of the final weights.

Fig. 4.4 shows the points in the tidal cycle at which water samples were taken. It also compares the tidal heights measured at these times with the predicted heights. There seems to be a discrepancy with the height of low tide at neaps. The difference reaches 0.5m, which is greater than variations caused by atmospheric pressure. This

has implications for the depths assumed when analysing the colour sensor data (§6.2).

4.2.2 August 1995

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This survey covered a neap-spring-neap cycle, 21 August-4 September. The transmissometer was fixed to the southern pier tower below low water (springs), but was the only instrument used for continuous monitoring. The water samples were taken at 14.00 hours to prevent shading from the pier itself, taking surface water to be analysed as before, plus near-bottom samples on four occasions. A total of thirteen water samples was analysed; five CS profiles, and eight Satlantic profiles (five of which could be used for reflectance) were taken.

The optical sensors took profiles through the water column at the same time as sample collection. During the first week, the CS24 measured upwelling and downwelling profiles, recording every 30 seconds, with another sensor measuring the ambient light every minute. There were problems with data logging on the CS24 so it was replaced by the Satlantic on Friday 25 August. The Spectron was used to measure surface and sub-surface reflectance as before, over the entire fortnight; this was prevented on 26 August due to rain.

In the laboratory, 3×11 were filtered for SPM concentrations, 3×250 ml for

pigment extraction, and 1×21 filtered to measure wet filter absorbance spectra,

although this was reduced to 11 when particle concentrations increased in the middle

of the survey. Water was filtered through membrane filters to determine yellow

substance using the UV 1201 spectrophotometer.

4.3 LOCH STRIVEN 1994

In April 1994, the RV Prince Madog undertook a survey in Loch Striven (Fig. 4.5), while two colour sensors and two fluorometers were deployed on a mooring. Loch Striven is a sheltered sea loch to the north of the Clyde Sea, and has been extensively used in phytoplankton studies (Tett, 1990). The instruments recorded data from 19 March until 20 April; they were then downloaded and returned to the mooring until 11 May 1994, with the cruise occurring over the turn around, 18-22 April. From the

ship, readings were taken with IRM1 and a profiling fluorometer; the water samples were analysed on board for SPM, chlorophyll concentrations and yellow substance.

The first survey in the Clyde Sea was in February 1994. The Clyde Sea (Fig. 4.5), or the Outer Firth of Clyde, is a fjordic sea loch extending from 55° 00'N to 56° 15'N, bounded by the Mull of Kintyre to the west, the Ayrshire coast to the east and the North Channel to the southwest. The total surface area is 3000 km², fed by a catchment area of 10500 km² which provides a total inflow of freshwater of ~ 340 $m³s⁻¹$. Thus, the low tidal currents (~0.1 ms⁻¹) result in almost permanent stratification

4.4 CLYDE SEA 1994 and 1996

(Walne, 1993).

Two profiles were taken at stations CS6 and CS8, to the east of Arran, with the IRMI, deployed from the RV Prince Madog. Water samples were also taken. Weather conditions prevented further data being collected.

The second survey was undertaken in June 1996 (Table 4.3). Optical measurements were taken with a Secchi disk and the PRR-600 while water samples were taken for concentrations and filter spectra. Two deep mooring stations were visited, and then six stations extending into the Clyde River to observe changes associated with salinity variations.

Cardigan Bay (Fig. 4.6) is the largest bay in the British Isles and has a high seasonal influx of cold water from the Snowdonia and Plynlimon Mountains. The bay shoals eastwards and shorewards, with a maximum depth of 50 m. Due to the irregular coastline of the northern shore, the tidal streams are asymmetrical, resulting in the ebb flow lasting $1\frac{1}{2}$ hours longer than the flood (Browne, 1993).

Table 4.3 Description of Clyde stations in 1994 and 1996 survey

4.5 CARDIGAN BAY 1994

Where the flooding saline water meets the freshwater a front is formed, usually in the vicinity of Hell's Mouth. The aim of this survey was to collect optical data from either side of the marked front. On the first attempt (24 June 1994), poor weather prevented the front from being identified, and data being collected. However, on the way back to Pwllheli, it was possible to take measurements in the lee of St. Tudwal's Islands. Two profiles were taken, plus water samples which were analysed later that day.

On the 30 June, there was a second attempt which proved more successful. Three profiles (with water samples) were taken on either side of the front. Unfortunately,

this was starting to break up due to the state of the tide. The water appeared clearer than that studied in the Menai Strait but with higher concentrations of particles than in the Clyde. The instruments used were those employed in the Menai Strait Survey.

4.6 VESTFJORDEN 1994

In September 1994, there was an opportunity to join the HMS *Herald*, on a survey to Vestfjorden, northern Norway. The fjord extends from 67°00' N to 68°30' N, and 12° E to 16° E, bounded by the Lofoten Islands to the west and the Norwegian coastline to the east.

measurements were taken are in Table 4.4. While on station, three instruments were deployed over the side of the ship: the Satlantic, a UCNW 4-channel colour sensor (CS2) and a profiling fluorometer. As these measurements were required to fit around the observations taken by the ship's crew the deployment of the optical instruments was not ideal. All sensors were lowered on the port side of the ship, regardless of the position of the sun. The winch for the Satlantic was also located near the bowthrusters which were necessary to maintain position throughout the cast, consequently the surface layers were usually disrupted by the expulsion of air through these ports. The colour sensor was lowered two metres aft of the Satlantic, and left in the water while the ship was on station to ensure that at least one reading was taken.

The survey positions are as shown on Fig. 4.7, and the sites at which optical

Unfortunately, this was sometimes affected by discharge from the galley and could not be pushed far from the ship's side as the bow continuously headed into the wind.

For each site, surface water samples were taken by lowering a bucket towards the stem of the ship, away from galley and laundry discharges. Where possible, samples were also taken from a depth of 10m on the ship's rosette sampler. The water samples were immediately taken to the ship's wet lab, where, for the surface water, 2 l were filtered for SPM and 3×11 were filtered for chlorophyll, the filtrate being collected and scanned in a 100 mm cell to measure yellow substance. An unfiltered surface water sample, which included all constituents, was also scanned with the

spectrophotometer. The water from the rosette sampler was limited, so that, for the

samples at depth, 21 were filtered for SPM with only 11 filtered for chlorophyll, and

a small sample scanned. The chlorophyll filters were put directly in 90% acetone and

left in a dark fridge for 24 hours before the acetone was refiltered and the filtrate

scanned against an acetone blank to gauge the chlorophyll concentration. Two drops

of HCl (conc) acid were then added and another spectrum taken. The SPM filters were left to air-dry and then stored until they could be oven dried in the Menai Bridge laboratory and weighed.

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Table 4.4 Description of Vestfjorden sites

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On the first day of analysis on board it was discovered that the 'distilled' water

included a sterilising agent which caused a yellow discoloration. From the second day onwards, the water was much improved but still gave unusual peaks in the spectra when used as a blank, so may have been affecting the optical measurements taken.

The first five days of the survey had relatively calm weather, with clear skies and sun on 1-2 October. However, the weather then deteriorated as the ship headed westwards and optical measurements were not possible. Unfortunately, the high swell and winds prevented further observations throughout the final five days of the survey.

4.7 CONWY ESTUARY (DOLGARROG) SURVEY 1995/1996

An estuarine environment was sampled as a contrast to previous sites, the estuary

having higher SPM concentrations and varying yellow substance. A pilot study was undertaken to assess the practicability of taking measurements from a bridge, and to monitor the change in yellow substance on the rising tide. This showed a marked change in g440 values and so was considered suitable. The survey itself was carried out at Dolgarrog Bridge (Fig. 4.8) on 27 July 1995.

As the water flowed inland, large quantities of foam and scum were apparent on the surface, possibly scoured from the banks downstream. Debris collected on the frame of the colour sensor, so limiting the downwelling light. It was not possible to remove the scum, so that for readings after 12:00 the sensor was partially obscured by debris

The instruments deployed were a UCNW 4-channel colour sensor (CS23), attached to a frame with floats so that the sensor pointed downwards at the surface (Fig. 4.9); a transmissometer, with depth sensor; a surface colour sensor (CS24) for ambient light measurement and the Spectron. The CS23 took readings every 30 seconds, with the

transmissometer reading every 10 seconds. Both instruments were lowered from the bridge and remained in the water between 11:00 and 14:00 BST. Water samples were taken at half hour intervals between $11:45$ and $13:15$, in conjunction with Spectron reflectance measurements. This period covered the flood tide, with the change in salinity indicating the influx of sea water.

on the surface.

The water samples were returned to the laboratory and analysed. Although enough water was collected for triplicate samples of 11 for SPM, the concentrations were too high for water to pass through the filter - consequently, the volume was decreased to 250 ml. The yellow substance was transported in dark glass bottles and then filtered and measured with the Diode-Array spectrophotometer. The filters for chlorophyll were frozen and analysed three weeks later when the fluorometer was available.

A second survey was undertaken on 26 March 1996, in which the profiling transmissometer was used, plus the PRR-600 - profiling so that attenuation could be calculated. Half hourly samples were taken between 14:00 and 16:00, on the flood tide. However, as the survey was done six days after spring tides the change in salinity was not observed, and the increase in water height was due to the backing of river water. The same laboratory techniques were used as above, except that the pigments were quantified immediately using the spectrophotometer rather than the fluorometer. Also, cell spectra were taken with and without a diffuser to study the particle scattering effects.

4.8 LLYN CWMYSTRADLLYN SURVEY 1995/1996

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A mountain lake provided further contrast to the marine surveys. This was expected to have little particulate matter, but some dissolved organics. Dwr Cymru kindly gave

permission for surveys in Llyn Cwmystradllyn, a reservoir on the southern flank of

Moel Hebog, Snowdonia (Fig. 4.10). Readings were taken from a tower situated 5 m into the reservoir accessed from the dam by a small bridge. Instruments were deployed from this walkway.

The same methods were employed as for the first Conwy survey, with the exception of the CS23. This profiled over 4 m, to calculate the vertical attenuation. On the first survey, 2 August 1995, the transmissometer was deployed but did not work, so there are no beam attenuation values.

Due to the lack of particulate material, over 11 of water was required for SPM

concentrations, limiting the analysis to duplicates rather than triplicates. The chlorophyll filters were frozen until 26 August when the pigment was extracted.

Once again, a second survey was undertaken, on 31 March 1996, following the same

structure as the second Conwy survey. As the water mass does not change in the lake on an hourly timescale, the instrument was turned upside-down to allow comparison between downwelling irradiance and radiance.

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Figure 4.2 Profile in Menai Strait 31/03/94
a) Transmittance a) Transmittance
b) Salinity b) Salinity
c) Temper Temperature

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Figure 4.4 Tidal curve for Pier Surveys
a) July 1994 a) July 1994
13

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b) August 1995

The dots show times at which daily samples were taken.

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day number $[21$ August - 4 September 1995]

Figure 4.5 Clyde Sea and surrounding area, Scotland

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Figure 4.9 Colour sensor with floats

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5.1 FIELD MEASUREMENTS

In situ measurements were made of diffuse attenuation K , reflectance R and beam attenuation c. These were taken so that Kirk's (1985) algorithms could be used to derive absorption and scattering which could then be compared with the laboratory measurements of absorption. In each survey, K and R were both measured with one

of the following instruments: IRM1, the CS instruments, the Satlantic or the PRR600.

There were fewer measurements of c as the transmissometer was not deployed in all

surveys. Methods for data collection and processing are given below.

5.1.1 Diffuse attenuation

where $S()$ is the sensor reading and z , d and $0⁺$ represent depth, dark and ambient (surface) readings respectively

value E cannot be given units, but indicates the relative change in irradiance. Therefore K can be calculated:

Before deployment a dark reading was taken with each light sensor - the cap remained on, or the sensor was covered to completely exclude the light, so that the background reading of the instrument could be determined. Then, light levels were measured at different depths in the water column to calculate K . The UCNW instruments required up to 2 minutes at each depth to record three readings which could then be averaged

for a representative value. The dark readings were subtracted from this measurement to compensate for the baseline value. Simultaneous measurements were taken of the ambient light level which were used to adjust for fluctuations in incident radiation.

The resultant light level $(E(z))$ at each depth was thus:

$$
E(z) = \frac{S(z) - S(d)}{S(0^+)}
$$

As these instruments had a relative calibration rather than an absolute calibration, the

$$
K = -\frac{\ln E_0 - \ln E}{z}
$$

The Satlantic and PRR600 can be programmed to take readings more frequently (e.g. one per second) and can therefore profile quickly, giving a more continuous record of the light field and thus, a more accurate calculation of K . With all instruments, it is necessary to measure the ambient light in order to distinguish between variations due

to the loss within the water and differences in incident radiation.

Measurements were taken on the sunny side of the ship/platform to minimise shading. This is particularly important from small boats where the shadow of the boat lowers light levels near the surface, but has no effect at greater depths, resulting in an apparent increase in irradiance with depth. The instrument will create self-shading, but as this is assumed constant throughout, the attenuation measurement will not be affected.

K was calculated as above, being the slope of the natural log of the subsurface measurements, as shown in Fig. 5.1. All values were divided by the relevant ambient reading when taken, but this was not always possible due to the use of different sensors. The near-surface measurements were excluded (for example the top 1.5 m) to prevent bias caused by noisy values due to surface wave disturbance, Fig. 5.2. The exclusion of data points was decided by inspecting the data and judging where error would be added. It was also important not to include readings close to the dark current of the instrument as these lower the attenuation values. These were omitted within the analysis program by setting a limit above the dark readings - this value was 15 for the IRM1 and 50 for the Satlantic and PRR-600.

When the sensor is pointing upwards the downwelling attenuation (K_d) is measured,

therefore upwelling (K_u) is recorded by turning the instrument over. K is similar for

upwelling and downwelling irradiance although the level of light is different. Fig. 5.3

illustrates this in the Pier Survey 1995.

The upwelling readings include all scattered and reflected light from objects at a greater depth, it is therefore important to calculate K_u where the influence of the bed or any subsurface structures is negligible - ideally, the depth of water should be greater than 6 attenuation depths $[6*(1/K_d)$ m (Aiken *et al*, 1995)].

The upwelling signal is also affected by self shading from the instrument itself. It is assumed that self-shading will be constant throughout the profile. However, the effect would be more pronounced near the surface, particularly in turbid water where the upwelling signal is greater due to the high number of particles scattering light back towards the surface. Consequently, the lack of downwelling light due to the sensor would significantly reduce the backscattered light upwards. This is particularly important for reflectance values.

5.1.2 Reflectance

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Reflectance values were taken to be the ratio between upwelling and downwelling irradiance immediately below the surface:

$$
R = \frac{E_{\omega 0}}{E_{d0}}
$$

as discussed in §2.2.2.

Light levels could not be accurately measured at the air-sea interface, so that upward and downward irradiance values were extrapolated from deeper measurements using K as calculated in §5.1.1. The ratio between the extrapolated value for the upwelling and for the downwelling irradiance was then used as reflectance at the surface.

For all readings with IRM1, the downward light was measured at several depths then the instrument was brought to the surface and turned over to measure upward light.

This meant there was a slight delay between upward and downward profiles, and an

allowance was included for the distance between the light sensor and the depth sensor.

Both the Satlantic and the PRR600 measured downwelling irradiance and upwelling

radiance L_{μ} . These are designed to correspond to satellite observations, but cannot be used to directly calculate subsurface irradiance reflectance, as discussed in §2.2.2. To avoid the unknown conversion factor, the instruments were used in their normal orientation and then inverted to measure upwelling irradiance and downwelling radiance. Although this enables the irradiance reflectance to be calculated, the upwelling values are close to the dark readings of the instrument and so may not be sensitive to changes. Unfortunately, the stronger downwelling radiance values saturated the Satlantic sensor in the surface 5 m. This problem was not encountered

with the UCNW instruments which are tolerant to a wider range of irradiance levels.

Above the water surface the Spectron was used to measure reflectance. This is calculated as the ratio between the signal from the surface of the water and the ambient cosine reading. Initially, the surface value was used, holding the Spectron I. m above the water, but this reading included a high proportion of interface reflectance, which dominated the signal emitted from the water. To eliminate this extra reflectance, the measurement was taken through a black pipe, covered to exlude sunlight, with one end held \sim 5 cm below the surface (Fig. 5.4). This method excludes the signal from the interface, measuring the upwelling signal within the water. As the pipe was 34 cm long, and the field of view was 15° from nadir, only -30 % of the signal was from the water; therefore, readings taken through the pipe must be multiplied by 3.33 to calculate the reflectance. Subsequently, measurements with and without the pipe were taken for comparison. The relationship between with and without pipe (see Appendix IV) has thus been calculated as:

 $R_{[no \; pipel]} = 0.36 R_{[pipel]}$

5.1.3 Beam attenuation

Two types of transmissometer were used to measure c: a profiling instrument in

Conwy and in the Menai Strait, and a fixed instrument in the Pier Surveys. Both dark and clear readings must be taken, V_{min} and V_{max} respectively, so that the voltages can be converted to transmittance (T):

The beam attenuation is then calculated:

 $\frac{c}{\sqrt{2}}$ ln $\frac{1}{\epsilon}$ $\frac{1}{\tau}$ = $a + b$ where l is the pathlength of the instrument, and a and b are absorption and scattering respectively

It was observed in the 1995 Pier Survey that when the transmissometer was exposed at low tide, the reading went to V_{min} instead of V_{max} as expected. This was due to water collecting on the ledge in front of the light source, and deflecting the beam away from the receptor (Fig. 5.5). This suggests that transmissometers should always be deployed in a vertical position when there is a possibility of exposure, as regular "clear" readings give a useful gauge of the degree of fouling each day.

Secchi disk readings were taken in most surveys. The Secchi depth z_{SD} is that at which the disk can no longer be seen when lowered into the water. At this point, the depth is gauged by markers on the rope. This parameter indicates the overall clarity, but the recorded depth is subjective, and can change with the viewer; it is also dependent on the reflectance and surface area of the disk (Edmondsen, 1980), the amount of shading and the state of the water surface (Tyler, 1968). However, it remains a workable estimate of clarity.

Laboratory analysis of the water samples was performed on the day of collection whenever possible. When delay was unavoidable, samples were stored in black bags and refrigerated overnight, or stored in a freezer for longer periods of time. This is not considered to affect the results (Tett, pers. comm.).

5.1.4 Secchi Depth

5.2 LABORATORY

5.2.1 Pigment extraction and determination

For each site, three replicates of 250 ml volume were filtered through Whatman GF/F filters (47 mm diam.) having shaken the samples to ensure they were well mixed. The filters were then immersed in 8 ml of 90% acetone in individual plastic centrifuge tubes, and refrigerated, in a black bag, for a minimum of 19 hours (usually 36) to ensure all pigment was extracted. If there was a delay in analysis the filters were desiccated, using silica crystals, and frozen before acetone was added. The tubes were centrifuged at 3000 rpm for 15 minutes, and the solution poured into a glass cell (rinsed with acetone), in which the fluorescence was measured with the Turner Fluorometer (f_0) . Two or three drops of 2N (8% by volume concentrated hydrochloric acid) were added for the determination of phaeopigments, and the fluorescence measured again (f_a) .

where K_f and H_f are instrument specific constants, v_e is extract volume and V is the volume of water filtered

The following algorithms were used to convert the fluorescences to pigment concentrations (Tett, 1990):

$$
C = K_f(f_o - f_a) \cdot v_d V
$$

$$
Ph = K_f(H_f f_a - f_o) \cdot v_d V
$$

$$
M = K_f H_f f_a - f_o \cdot v_d V
$$

For the surveys in 1996, the fluorometer was not available so the pigments were measured with the spectrophotometer. The pigments were extracted in the same way as above, then the solution was poured into a 10 mm cuvette and the spectrum measured against a blank of pure acetone. Drops of acid were added and the spectrum taken again, against a blank of acidified acetone.

The appropriate algorithms for this method are (Parsons *et al*, 1984):

\n
$$
\text{Ch1-a} = 11.85 \, A_{664} - 1.54 \, A_{647} - 0.08 \, A_{630}
$$
\n

\n\n $\text{Ch1-b} = 21.03 \, A_{647} - 5.43 \, A_{664} - 2.66 \, A_{630}$ \n

\n\n $\text{Ch1-c} = 24.52 \, A_{630} - 1.67 \, A_{664} - 7.60 \, A_{647}$ \n

\n\n the sheakrona at the subgraph is calculated by the above the value of the above.\n

where A is the absorbance at the subscript wavelength minus the absorbance at 750 nm

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The chlorophyll concentrations are then calculated:

$$
C \left(mg \text{Ch/m}^{-3} \right) = \frac{Chl * v}{V * l}
$$

where v is the volume of acetone used in ml, V is the volume of seawater in V litres and 1 is the length of the cuvette in cm

where the subscripts o and a represent the reading before and after the addition of acid, respectively, absorbances corrected to 750 nm

Phaeopigments can then be calculated:

$$
Ph = \frac{26.7 [1.7 (665)] + (665) + v}{V * l}
$$

When in Vestfjorden, it was not possible to follow either of these procedures. A litre of water was filtered initially, and the pigments extracted in acetone as before. After the tubes were taken out of the fridge, the filter/acetone was transferred to a clean syringe and the liquid forced through a Whatman GF/C filter. The filtrate was put in a 10 mm cuvette and scanned between 350 and 750 nm in the UV-1201 Spectrophotometer. This was compared with a blank of pure acetone. HCl acid was

again added to determine phaeopigments.

meant that all absorption was measured whereas if membrane $(0.2 \mu m)$ filters were used, the absorption by particles between $0.2 \mu m$ and $0.7 \mu m$ would have been omitted. However, when comparing these data with other surveys (some of which use GF/F, and some membrane filters) the particular definition of "yellow substance" must

5.2.2 Yellow substance

The absorbance of the filtrate (from the above filtration, using GF/F filters) was measured between 300 and 800 nm in a spectrophotometer, against a blank of distilled water. 100 mm cells were necessary to detect the dissolved organic matter/humic acids. Membrane filters could be used instead of GF/F filters to eliminate smaller particles but a comparison showed that GF/F filters were adequate for the levels present during the summer (see Appendix V). A greater difference would be observed during the winter but GF/F filters were nevertheless used for consistency. This also

be considered.

The absorbance value at 750 nm (a750) was taken to represent scattering. This is necessary as water and inorganic particles are the only significant absorbers at 750 nm (Gallegos *et al*, 1990) - the effect of water is removed by use of the blank, and the particles have been removed by the filtering so that any signal is due to scattering by particles small enough to pass through the filter. Thus, a750 is subtracted across the spectrum (assuming the effect of scattering is uniform) before converting absorbance

into absorption. The conversion algorithm used to obtain the absorption coefficient from the measured absorbance was:

$$
a(\lambda) = \frac{\ln(10).A(\lambda)}{I}
$$

where $a(\lambda)$ is absorption, $A(\lambda)$ is absorbance and *l* is the cell length in m

Yellow substance was then quantified by the absorption value at 440 nm (g440).

5.2.3 Seston

One litre of well mixed water from each site was filtered through pre-rinsed, -ashed

and -weighed GF/F filters, followed by 300-500 ml distilled water to remove any salt. The amount of water for rinsing was based upon a comparison of measurements using different volumes of water, and taking the volume which resulted in the lowest weight (Fig. 5.6). The filters were dried overnight at 80°C, and weighed with the same balance that was used initially. This gave the total seston weight and thus concentration. Filters were then furnaced at 500° C for three hours and re-weighed to quantify inorganic particles (Parsons et al, 1984).

For several sites, the water was filtered through two filters, one on top of the other, the bottom filter acting as a blank. This underwent the same drying and weighing

techniques as the top filter to assess errors within the method. The final weights from these were variable, and although usually below 0.4mg the highest value was 5.5 mg. In general, this error was 10% of the total value; for example, during the July Pier Survey, between 16 and 19 July, the total seston on the "top" filters weighed 3.14 mg,

3.76 mg, 3.99 mg and 3.41 mg while the "blank" filters weighed 0.26 mg, 0.48 mg, 0.58 mg and 0.37 mg respectively.

The addition of an extra filter below another meant that the filters were handled more and could lead to greater error. It is therefore preferable to do triplicate samples with a greater volume of water and gauge any measurements error from the variability between these, so using the average for the final value. This technique was used in the later surveys, Conwy Estuary and Llyn Cwmystradllyn, when three 11 replicates

were filtered for seston. The average value from these gives a more accurate concentration as well as gauging natural variability.

5.2.4 Spectra

Spectra of water samples and particles on filters were taken, using the Hewlett Packard Diode-Array spectrophotometer for November 1993-June 1994, and thereafter with the SHIMADZU UV-1201. It was found that there was less "noise" in the SHIMADZU spectra.

In November 1993, the range taken was 400-700 nm, but this was extended to 300-

800 nm to observe variations due to organics (Bricaud et al, 1981) in the ultra-violet

and scattering within the near infra-red.

The absorbance spectra of liquids were taken in a 100 mm glass cell, with a distilled water blank. The scan was downloaded onto computer disk. To convert the absorbance measured by the spectrophotometer to absorption, the procedure previously described for yellow substance was followed. Both the spectra of the filtrate and the untreated water samples were measured in this way.

Particles were scanned on GF/F filters (having been filtered as above). These were

saturated with distilled water and placed on a glass slide, which was then positioned over the detector (see Appendix VI for a comparison between the filter over detector and source), and scanned between 300 and 800 nm. A clean filter saturated with distilled water was used as a blank. Spectra were taken of 'dried' and furnaced

particles for all surveys, and fresh filters in January 1994, June 1994, and the Menai Pier Surveys. The absorption coefficient was then calculated:

$$
a(\lambda) = \frac{\ln(10).A(\lambda)}{V/\text{area}}
$$

where V is the volume of water filtered and area is the area of the filter which is covered with particles

Various pathlength amplification factors, as discussed in §2.3.1, were applied to the

measurements and then compared.

5.3 SUMMARY

The measurements were thus split into two distinct categories - the observation of apparent properties in situ and inherent properties in the laboratory. Consequently, in the field the upwelling and downwelling diffuse attenuation was measured, and then used to calculate the irradiance reflectance at the surface. In some instances, beam attenuation was also measured. Water samples were then taken back to the laboratory in order to measure the spectral absorption due to the water itself, the yellow

In the field, error was added by the time lag between the measurement of upwelling and downwelling attenuation, plus instrument shading. In the laboratory, the pathlength amplification factor present in filter measurements added uncertainty to the value of absorption, while solutions allowed particles to settle. To enable the comparison between the field and laboratory measurements, inherent-apparent relationships have been used which were developed by Kirk (1985), but due to the large uncetainties in the applicability of these equations more general relationships were also used, plus various values for the pathlength amplification factor including

the variation calculated by Cleveland and Weidemann (1993) and a constant value of

2.

These adjustments were performed to all values to identify if the agreement between the in situ and laboratory measurements was improved when a particular combination was used, so confirming the appropriate corrections for that survey.

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Diffuse attenuation: slope of ln(irradiance) at 555 nm Figure 5.1

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Figure 5.2 Noise near surface in irradiance profile at 555 nm (AMB95)

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<u>က္</u> \overline{S} Figure

7 O with \bullet Spectron the bf drawing Schematic

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Transmissometer, with beam deflected by water on ledge of instrument Figure 5.5

Weight when filters rinsed with different volumes of distilled water, $n=3$ for each point Wate Dellited **O50** ┯ $\overline{\sigma}$ \bullet amount **Sept.**

6. FIELD RESULTS

All results are tabulated in Appendix VII.

Both the inorganic solids and the pigment concentrations showed seasonal variation during the Menai Strait Survey (Fig. 6.1). Pigment concentration remained below 1.5 mgm⁻³ during the winter, and then peaked in May and June, with 18.7 and 14.1 mgm³ respectively. Conversely, the inorganic particle concentrations were greatest during November and December, reaching 35 mgl''. This was attributed to increased wind stirring combined with greater mobility of the mineral particles due to decreased binding by organics. Yellow substance did not show any trend in variation, during the Strait survey, remaining at -0.3 m⁻¹.

Vestfjorden had the lowest concentrations, with pigments below 0.2 mgm³ and yellow substance less than 0.35 m^1 . The Clyde Sea had a similar level of yellow substance (~ 0.35 m⁻¹ in 1994) decreasing to 0.089 m⁻¹ in 1996 when the membrane technique of measurement was used. Pigment concentrations were still low, varying from 0.8 mgm⁻³ in 1994 to 1.0 mgm⁻³ in 1996, while inorganic concentrations increased from 0.25 mgl^{-1} in 1994 to 2.49 mgl⁻¹ in 1996. A significant increase in all constituents was measured within the Clyde Estuary, with maximum concentrations of 1.57 m⁻¹ and 4.55 mgl⁻¹ for yellow substance and MSS respectively at CE6 (the station furthest inland), and a maximum of 3.15 mgm⁻³ for pigments at CE3.

Yellow substance varied between 0.248 m^{-1} and 0.588 m^{-1} in Cardigan Bay, with low pigments $(0.09-0.77$ mgm⁻³) but relatively high inorganic concentrations $(5.1-9.1)$ mgl⁻¹). Values for yellow substance were similar in Llyn Cwmystradllyn (0.28-0.40 $m⁻¹$) combined with low pigment and MSS concentrations (1.1-2.2 mgm⁻³ and 1.3-4.0

mgl⁻¹ respectively). These concentrations are indicative of the nature of the lake, *i.e.*

6.1 CONSTITUENT CONCENTRATIONS

there is a low contribution from run-off due to the situation in a mountainous area,

leading to low levels of particulates and terrestrial humic acid.

In both the July Pier Survey and Loch Striven a phytoplankton bloom was observed, reaching chlorophyll concentrations of 8.51 and 43.8 mgm⁻³ respectively. The Loch Striven data also showed higher values of yellow substance (0.29-0.56 m') suggesting that the phytoplankton contributed a detrital component to the humic acids.

In the August Pier Survey (1995), the inorganic concentrations followed a springneap tidal cycle, being greatest at spring tide (10.25 mgl^{-1}) , decreasing to 1.01 mgl⁻¹ at neap tide. Although yellow substance varied considerably during this period (0.092-0.405 m'), the variation did not directly follow the spring-neap cycle.

The highest concentration in all constituents was found in the Conwy River: pigments 10.4-56.1 mgm⁻³, yellow substance 1.7-3.8 m⁻¹, 18-164 mgl⁻¹ for TSS, and 12-136 mgl⁻¹ for MSS.

A wide range of K_d values occurred across the various sites (Fig. 6.2). Seasonal variation was again apparent in the Menai Strait, resulting in a total range of K_d from 0.4 to 3.5 m'. Vestfjorden was the clearest water body, with values of 0.115-

0.272.m⁻¹; this was expected as these sites were in Case 1 waters. However, both the Cardigan and Clyde Sea results were of a similar magnitude, with K_d less than 0.4 m⁻¹ at 443-444 nm. Loch Striven, the Pier Surveys and the Strait Survey all reached higher values, with the upper limit indicating the total amount of seston present (see §5.1.1). Similarly, the maximum value at 440 nm observed in the Clyde Estuary was 2.26 m^1 at CE6, corresponding to the higher concentrations of constituents.

6.2 DIFFUSE ATTENUATION

Fig. 6.5 shows the change in attenuation throughout the year in the Menai Strait. The high values in November and December 1993, 1.5< K_d < 3.5, decrease through

The decrease in irradiance observed in Vestfjorden illustrates Eqn 2.1 very well, following an exponential curve (Fig. 6.3). The comparison of this decrease across the

spectrum shows how the longer wavelengths attenuate faster in clear water (Fig. 6.4).

the spring and summer to $K_d \sim$ 0.5 m' in August 1994, before increasing in October. The values at 552nm are given in Table 6.1 to show the typical variation at a particular wavelength; as all channels co-varied, these values are representative of the whole spectrum.

Table 6.1 K_d (m⁻¹) values at 552 nm for the Menai Strait Survey 1993-1994

The consistency of the spectral shape in the Menai Strait is illustrated in Fig. 6.6a-d where each channel is compared to the reading at 596 nm (overall minimum). This shows the attenuation at short wavelengths is most variable, although still with a high correlation (r^2 = 0.91). The slope in all four correlations is greater than 1, which indicates that the attenuation at 596 nm will become an increasingly marked minimum as the overall magnitude rises. The negative intercepts for the 521 and 552 nm channels indicate that at low values of K_d (clear water) the minimum will shift to lower wavelengths. A characteristic spectrum for the Menai Strait can therefore be

derived by normalizing the spectra; this is shown in Fig 6.7.

The attenuation values for the Pier Surveys were less accurately determined. In July

1994, the IRM1 was used on eight days, although two of these were badly affected

by shadow and were therefore considered void. The CS sensors were deployed throughout this survey, but as readings were only taken every 30 minutes, attenuation could not be calculated over a short period of time. The best estimates needed to use readings over the entire day, which removes any short term variation, $K_d(570)$ increasing from 0.386 $m⁻¹$ on 13/07/94 to 0.874 $m⁻¹$ on 19/07/94, before decreasing again. Fig. 6.8 shows how the values of K_d from the different instruments vary, and the increase in error over shorter periods due to fewer readings.

The following year, the profiling CS24 was used to measure K_d , recording every 30 seconds. However, due to a malfunction in the pressure sensor the instrument switched itself off at various times under the water, limiting the usefulness of the readings. After five days, this was replaced by the Satlantic, but unfortunately, this would not download on two occasions, giving a total of eight profiles over the survey.

As the colour sensors were taking measurements over the whole fortnight, they were useful for monitoring changes in the level of irradiance at set positions. The bottom sensor CS4 clearly shows a tidal signal (Fig. 6.9). At neaps there is an increase in irradiance towards the middle of the day, this is due to the increase in ambient irradiance, and also the decrease in tidal height. At spring tides there was a clear duality in the signal, with peaks early in the morning and late in the afternoon; the decrease during the middle of the day is caused by the increased water column above the sensor at high tide (Fig. 6.9). Similarly, the tidal signal can be identified in the 490: 570 ratio at the bottom (Fig. 6.10). The ratio decreases as the tidal height increases, as light at 490 nm is attenuated faster than that at 570 nm. The 490:570 ratio remains constant throughout the survey both for the surface sensor and the upwelling light sensor, confirming that this change in signal is due to the height of the water column and not changes in the ambient radiation or constituent concentrations.

In addition, the surface sensor was not sensitive enough, nor recording at short enough

intervals to be equivalent to the sub-surface sensors, so that ambient changes could

not be removed from the underwater data.

The August 1995 Pier Survey shows that K_d at Menai Bridge (Station 5 in the Strait

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Survey) was similar the next year, 0.4 -1.2 m⁻¹, although extending over a wider range than August 1994 as the readings were taken over a full spring-neap cycle. Measurements over the two-week period identified a tidal signal, with K_d being highest at neap tides (Fig. 6.11).

As the water body did not change in Cwmystradllyn, it was possible to do a series of profiles over time, showing that the attenuation did not change throughout the day,

and studying the relative diminution of different wavelengths with depth. This is clearly shown with the change in the 440:570 ratio in Fig. 6.12, and illustrates the phenomenon observed in the Pier Survey.

6.3 REFLECTANCE

There was a detectable trend in the colour sensor R through the July Pier Survey (Fig. 6.15), which does not coincide with the attenuation trend, as the signal continues to increase until 22/07/94, and then remains constant rather than decreasing after 19/07/94 as K_d did. Unfortunately, there were not enough readings with IRM1 to confirm this trend.

No trend was observed in reflectance during the Menai Strait Survey (Fig. 6.13). This may be due to the difficulty in measuring upwelling irradiance which is so low that it was near the threshold of the instrument, particularly for the winter readings. The range of ambient light levels is shown in Fig. 6.14, illustrating- the marked difference between winter and summer conditions. The blue and red channels were most affected as these had the greatest attenuation values. On inspection of the data, there seemed to be slightly lower values of R during the summer (May-August), but the high variability of the measurements prohibits any clear distinction.

The Spectron reflectance values do not show any clear progression through the first

week of the July survey either. However, in 1995 the Spectron indicated an increase

from 7.3 % initially to 26.3 % on 31/08/95. The reflectance calculated from the

Spectron and that from the Satlantic (assuming the conversion between L_{μ} and E_{μ} is π) do not correlate well (Fig. 6.16).

The lack of pigment in Cwmystradllyn limits the level of reflectance, with only a small peak between 550 and 600 nm (Fig. 6.17). However, as the water body did not change, the lake was used to study the relationship between E_u and L_u (Fig. 6.18). This comparison suggests the relationship:

$$
E_{\nu} = 3.29 L_{\nu}
$$

close to the value of π used for a Lambertian surface (see §2.4.1). This constant

implies a lack of directionality in the light field which was confirmed by tilting the sensor and observing only small changes with angle (Fig. 6.19).

There is a marked difference in the shape of the reflectance spectrum at Cwmystradllyn and that observed at Dolgarrog (Fig. 6.20). The high concentration of sediment in the Conwy results in a shift of maximum R to longer wavelengths, giving the water a reddy-brown appearance. This illustrates that the absorption increased at the blue end of the spectrum due to yellow substance and sediment.

The Secchi depths (z_{SD}) observed in the Menai Strait clearly support the diffuse attenuation data (Fig. 6.23), as the depth increases from 1.6 m in March to 4.25 m in August.

This shift in the maximum to longer wavelengths was seen more gradually in the spectra from the Clyde (Fig. 6.21) where CS1 and CS4 are in the Clyde Sea, with low reflectance, while CE3 and CE5 are taken in the estuary, showing a higher level of reflectance with the peak further towards the red.

The effect of bottom reflectance can be seen in the profiles from Cwmystradllyn (Fig. 6.22a and b) and Dolgarrog (Fig. 6.22c and d). R is expected to decrease exponentially with depth (Kirk, 1994) whereas in these surveys the reflectance increases near the bottom. This is due to the more penetrating wavelengths being reflected upwards from the bed. This highlights the need for a larger water column to ensure that light is not reaching the bottom.

6.4 SECCHI DEPTH

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Through the Pier surveys a tidal signal was observed. During the July Survey (Fig. 6.24) neither the spring-neap nor the diurnal tidal signal were clearly shown in the Secchi depths. However, in August 1995 the spring-neap cycle is obvious in the observed depths (Fig. 6.25), with values of 4.25 m at neap tides to 1.4 m at springs.

6.5 BEAM ATTENUATION

During the Menai Strait Survey a transmissometer was used on only one occasion from the Sandpebbler, to confirm that the column was mixed. This was taken on 31/03/94 from 07:30 to 09:00 as the tide turned. The results have already been shown in Fig. 4.3. However, a transmissometer was deployed for both Pier surveys.

There was a greater range in attenuation in August 1995, extending from 2 m⁻¹ on 21/08/95 to 9 m^{-1} on 29/08/95 on the neap-spring succession (Fig. 6.27), and then declining to \sim 5 m⁻¹. The readings at the end of the deployment were higher than the initial measurements of attenuation due to fouling of the instrument. Once again, the

The highest values of attenuation were observed in the Conwy, \sim 50 m⁻¹ corresponding to 1% transmittance. This coincides with the tidal front passing the bridge (Fig. 6.28). The beam attenuation then decreased again after the front had

In July 1994, the transmissometer stopped recording after six days limiting the readings to those taken at midday which was noted manually when taking the other optical measurements. However, from 11/07/94 to 17/07/94 the attenuation increased from 1 $m⁻¹$ to 3 $m⁻¹$ corresponding to the development of an algal bloom (Fig. 6.26). On each day a semi-diurnal cycle is apparent, c being greatest at high tide, which is superimposed on the general trend. The midday readings for the remainder of the survey confirm the subsequent decline in attenuation to the initial level observed as the phytoplankton concentrations decreased. The tidal signal was not mirrored in the temperature readings, although the increase to 18/08/94 was apparent, suggesting that the phytoplankton bloom dominated the properties of the water column.

semi-diurnal cycle was apparent.

passed and the salinity of the water increased.

6.6 DERIVATION OF a AND b

Kirk's algorithms (1985) were applied to K_d and R as described in §2.4.2 to derive a and b. Fig. 6.29 shows the variation over the whole year from the IRM1 data in the

Menai Strait. Even though R did not show a seasonal trend, the change in K_d resulted in a decrease in b from winter to summer, corresponding to the decrease in

In August 1995, the Satlantic results in values of c which are much lower than that measured with the transmissometer. However, when the Spectron reflectance was used in conjunction with the Satlantic K_d , the agreement was much better (Fig. 6.31b).

TSS (see §5.1). In the July Pier survey, the derived absorption follows the trend of diffuse attenuation (Fig. 6.30a and b), with a maximum value on 19/07/94, whereas scattering increases until 22/07/94. This trend is apparent when using values calculated over the whole day or only 2 hours (Fig. 6.30c and d), suggesting that these are real progressions and illustrating the stronger dependences between absorptionattenuation, and scattering-reflectance.

In both Pier surveys, $a+b$ can be compared with c to test the validity of the Kirk algorithms in this environment. In July (Fig. 6.31a), both the colour sensors and IRM1 agree in magnitude with the transmissometer, but neither shows the same trend.

To determine the specific values of absorption and scattering for each constituent *in* situ, the derived values of a and b can be regressed on the concentrations. The absorption value for water must first be removed, and then a multiple regression on yellow substance, pigment and inorganic concentrations can be performed. If there are not enough data points for a particular site, and one constituent dominates the

6.7 DERIVATION OF a* AND b*

signal, an approximate value can be reached by dividing the absorption (minus water) by the concentration.

In the Menai Strait, yellow substance did not vary significantly, and therefore cannot be extracted through regression, so must be considered as a constant, giving the

equation:

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$$
a - a_w = a_{const} + a_c^* C + a_m^* M
$$

The absorption and scattering values for sea water at relevant wavelengths are given in Table 6.2.

The results from a regression of pigment and MSS concentrations on the Menai Strait

IRM1 $a-a_w$, are given in Table 6.3.

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inorganic concentrations for the Menai Strait survey

This regression can be undertaken for each survey. The resultant specific absorption

and scattering coefficients are given in Table 6.4 and 6.5 respectively.

(nm) $\boldsymbol{\lambda}$	410	440	490	510	520	550	600	670
\bullet a_c								
MS	\bullet	0.011	\bullet	\blacksquare	0.009	0.004	0.005	0.002
MP	0.4125	0.4140	0.2852	0.3288	\blacksquare	0.3253	$\qquad \qquad \blacksquare$	0.3438
Clyde	0.0569	0.0052	-0.0043	-0.0031	$\qquad \qquad \blacksquare$	-0.0051	\bullet	0.0118

concentrations on derived absorption

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Table 6.5 Specific scatter for each constituent at all sites from the regression of concentrations on derived scatter

The great range in coefficients and the presence of negatives show that this regression technique only applies when a greater number of points are included. However, the mixture of concentrations from different locations will be less effective in identifying the characteristic spectra of different water bodies.

6.8 DISCUSSION

The constituent concentrations and the optical properties show similar trends

confirming the dependence of the water colour on the constituents. When the mineral solid concentrations are high there is a corresponding increase in diffuse attenuation. The increase in MSS in the winter in the Menai Strait indicates that the mineral particles are freer to move around without the organic binding which is present during the warmer months. The higher number of particles results in more photons being intercepted, and thus higher scattering and absorption.

The range of K_d values was shown in Fig. 6.2. The linked increase in particle concentrations and K_d is also apparent in the shape of the attenuation spectra. The spectral shape of K_d changes with overall magnitude (Fig. 6.32). At low values, minimum attenuation occurs between 500 and 550 mn, with a slight increase towards the blue and a much greater increase in the red. As the value of K_d becomes greater, the minimum shifts to longer wavelengths (550-600 nm), while the blue attenuation exceeds the red. This change in shape represents the shift from water dominating the signal with high absorption in the red, through an increase in dissolved organics which absorb in the blue (Fig. 6.33), to particles which absorb more in the blue and increase overall scattering.

It is also apparent that the optical properties covary due to their dependency on the constituents, particularly z_{SD} and K_d . Comparison of z_{SD} with K_d (Fig. 6.34) gives a

correlation for the Menai Strait survey and Cardigan Bay (using K_d at 552 nm) of:

$$
\frac{1}{K} = 0.926 z_{SD} - 0.148 \qquad \qquad r^2 = 0.636 \qquad n = 80
$$

where the constant is significantly different from zero.
If the PAR sensor is considered (used during ANIB95) the relationship improves to:

$$
\frac{1}{K} = 0.588 z_{SD} + 0.242 \qquad \qquad r^2 = 0.804 \qquad n = 11
$$

Although there is a strong relationship between K_d and z_{SD} neither of the above regressions agree the relationship discussed in §2.4.2 (Holmes, 1970) of $K_a = 1.44/z_{sn}$.

However, it is possible to compare z with $c+K_d$ (Fig. 6.35), using either the Kirk derived $a+b=c$ or the transmissometer reading for c.

In the Menai Strait Survey there is good agreement when using $a + b$ correlating as

$$
\frac{1}{(c+K)} = 0.216 z_{SD} - 0.204 \qquad r^2 = 0.587 \qquad n = 51
$$

The relationship is improved when the values for Cardigan Bay and the Clyde 1996 are included plus the Pier survey readings, using the transmissometer c:

$$
\frac{1}{(c+K)} = 0.251 z_{gD} - 0.283 \qquad r^2 = 0.811 \qquad n = 69
$$

The correlation improves further when PAR attenuation is used (Fig. 6.36):

$$
\frac{1}{(c+K)} = 0.060 z_{SD} + 0.019 \qquad \qquad r^2 = 0.865 \qquad n = 10
$$

Again, these show a good correlation between z_{SD} and $(c+K_d)$ but do not agree exactly

with the values from the literature discussed in §2.4.2.

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In previous studies, yellow substance has been related to salinity (see §2.4.3). This

was tested in the Clyde Sea/Estuary survey (Table. 6.5). A good correlation was found (Fig. 6.37), even when sites which were beyond the influence of the estuary were included:

$\textit{Sal} = 34.95 - 11.977 \text{ } YS \qquad T^2 = 0.982$

which confirms that yellow substance can be used as a conservative tracer in this location.

6.9 SUMMARY

In general, the variation in constituent concentrations and apparent optical properties

were related. The spectral shape of K_d changed as the magnitude increased indicating the change in the dominant constituent, with the increase in sediment resulting in an overall higher value and, more specifically, an increase in the blue.

A good correlation was found between z_{SD} and $(c+K_d)$, as well as confirmation that yellow substance could be used as a tracer for salinity. The use of optics to monitor salinity variation within estuaries would be a useful progression.

Reflectance was less clearly linked with the constituents but this may be due to errors within the measurement. It was also difficult to derive specific absorption and scattering coefficients for each survey due to the limited number of samples, although for the more intensive surveys such as the August Pier Survey and the Menai Strait Survey this was possible. For future studies, this would be a good way of distinguishing, the dominant optical parameters at any particular location.

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Table 6.5 Yellow substance concentrations and salinities for stations in the Clyde Sea, Estuary and surrounding lochs, 1996

Figure 6.1 Concentrations for Menai Strait Survey

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Figure 6.2 Diffuse attenuation ranges at 443-444 nm at different sites

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Figure 6.3 Irradiance profile at 555 nm (Vestfjorden)

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Figure

Figure 6.5 Diffuse attenuation at all sites for each month in the Menai Strait

- $\frac{\text{Survey}}{\text{a}}$
- a) 444 nm
b) 521 nm
- b) 521 nm
c) 552 nm c) 552 nm
d) 596 nm
-
- d) 596 nm e) 670 nun

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month 1993-1994

Figure 6.6 Consistency of spectral shape of K_d in Menai Strait Survey, comparing each IRM1 channel with the value at 596 nm
a) 444 nm against 596 nm

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- a) 444 nm against 596 nm
b) 521 nm against 596 nm
- b) 521 nm against 596 nm
c) 552 nm against 596 nm
-
- c) 552 nm against 596 nm
d) 670 nm against 596 nm d) 670 nm against 596 nm

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 K_d for July Pier Survey 1994, calculated from different instruments
a) colour sensor: all readings Figure 6.8

-
- colour sensor: 12:00-14:00 GMT $b)$
- IRM1 $c)$

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JMB94 level of light (570 nm) at bottom colour sensor showing Figure 6.9 variation with height of water column through tide: spring tide 11/07/94, neap 17-18/07/94

12-15 July. $a)$ 16-18 July $b)$ 19-21 July $c)$ 22-25 July d)

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 $\sim 10^{-10}$ km s $^{-1}$. \mathcal{L}_{max} , where \mathcal{L}_{max} $\mathbf{q} = \mathbf{q}$, and $\mathbf{q} = \mathbf{q}$ $\mathcal{O}(\mathbb{R}^d)$. We set $\mathcal{O}(\mathbb{R}^d)$ $\mathbf{S}^{(n)}$ and $\mathbf{S}^{(n)}$ $\mathcal{A}(\mathbf{c})$, and $\mathcal{A}(\mathbf{c})$ \mathbf{r} .

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Figure 6.10 JMB94 490:570 ratio at bottom sensor showing change with tidal cycle, from low values at midday with spring tides, with a peak at midday for neap tides

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11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

date July 1994

July Pier Survey 1994: diffuse attenuation calculated from colour sensor readings for the whole day Figure 6.11

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 $\mathcal{M}_{\rm{max}}$

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11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

date July 1994

Figure 6.12 Cwmystradllyn [02/08/95] 440:570 variation through water column, . Indicating relative decrease in blue light to green light $\frac{1}{2}$

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Figure 6.13 Reflectance values for Menai Strait Survey
a) 444 nm

- a) 444 nm
b) 521 nm
-
- b) 521 nm
c) 552 nm
- c) 552 nm d) 596 nm ··
e) 670 nm e) 670 nm $\mathcal{L}^{\text{max}}_{\text{max}}$

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Figure 6.15 Reflectance values for July Pier Survey 1994
a) colour sensor 12:00-14:00 GMT a) colour sensor 12:00-14:00 GMT
b) Spectron SE-590 spectra

Spectron SE-590 spectra

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wavelength nm

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Figure 6.18 Upwelling signal measured by Satlantic for Cwmystradllyn [31/03/96] a) upwelling radiance L_u and irradiance E_u b) ratio between irradiance and radiance

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Figure 6.19 Variation of radiance with angle in Cwrnystradllyn [31/03/96]
a) tilt/roll angle and radiance over time a) tilt/roll angle and radiance over time
b) radiance level against tilt angle radiance level against tilt angle

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 $\sim 10^{11}$ km s $^{-1}$

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secs after start [10:41]

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Reflectance $\%$

 \mathbf{L}_{c}

Figure 6.22 Effect of bottom albedo in reflectance profiles, assumes E=L π
a) Cwmystradllyn 31/03/96: 412 nm, 443 nm, 490 nm

- a) Cwmystradllyn 31/03/96: 412 nm, 443 nm, 490 nm
b) Cwmystradllyn 31/03/96: 510 nm, 555 nm, 665 nm b) Cwmystradllyn 31/03/96: 510 nm, 555 nm, 665 nm
c) Dolgarrog 26/03/96: 412 nm, 443 nm, 490 nm
- c) Dolgarrog 26/03/96: 412 nm, 443 nm, 490 nm
d) Dolgarrog 26/03/96: 510 nm, 555 nm, 665 nm
- Dolgarrog 26/03/96: 510 nm, 555 nm, 665 nm

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reflectance X

Secchi depth measured through the July Pier Survey 1994 Figure 6.24

- Daily value at midday with tidal height $a)$
- $b)$ Hourly value through 24 hour period 21-22 July, with tidal height

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2.$ \mathcal{L}_{max} and \mathcal{L}_{max} .

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date July 1994

 $time 21-22$ July 1994

Figure 6.25 Secchi depth measured through the August Pier Survey 1995

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 $\mathbf{x} \in \mathbb{R}^n$ \sim $\mathbf{x} = (x_1, \ldots, x_n)$ $\mathcal{S}(\mathcal{S})$, and $\mathcal{S}(\mathcal{S})$

date August-September 1995

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235 237 239 241 243 245 247 233 day number [21 August - 4 September 1995]

Figure 6.26 Transmissometer readings through tidal cycle, July Pier Survey 1994
a) beam attenuation

- a) beam attenuation
b) temperature
-
- b) temperature
c) tidal height tidal height

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 $\label{eq:2.1} \frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1$ $\mathcal{A}(\mathbf{r})$

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Transmissometer readings through tidal cycle, August Pier Survey 1995 Figure 6.27

- beam attenuation: all readings $a)$
- beam attenuation: de-spiked and averaged per hour $b)$
- tidal height $c)$

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 $\mathbf{X} \in \mathbb{R}^{n \times n}$

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August-September (32+) 1995 date

Transmissometer readings through flooding tide at Dolgarrog, Conwy Figure 6.28 beam attenuation $a)$ salinity $b)$

- temperature
depth of sensor $\mathbf{c})$ d)
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 $\label{eq:2} \frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1$ $\label{eq:2.1} \mathcal{L}(\mathcal{L}(\mathcal{L})) = \mathcal{L}(\mathcal{L}(\mathcal{L})) = \mathcal{L}(\mathcal{L}(\mathcal{L})) = \mathcal{L}(\mathcal{L}(\mathcal{L}))$

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Figure 6.29 Absorption and scatter derived from IRM1 readings for Menai Strait Survey using Kirk's (1985) algorithms
a-e) absorption coefficient 444 nm, 5

absorption coefficient 444 nm, 521 nm, 552 nm, 596 nm and

670 nm

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Figure 6.29 Absorption and scatter derived from IRM1 readings for Menai Strait

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Survey using Kirk's (1985) algorithms
f-j) scattering coefficient 444 nm, 521 \mathcal{L}_{\bullet} scattering coefficient 444 nm, 521 nm, 552 nm, 596 nm and 670 run

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Figure 6.30 Absorption and scatter derived from colour sensor readings for July Pier

- Survey 1994 using Kirk's (1985) algorithms
a) absorption from colour sensor reading a) absorption from colour sensor readings all day
b) scatter from colour sensor readings all day
-
- b) scatter from colour sensor readings all day
c) absorption from colour sensor readings 12:0 c) absorption from colour sensor readings 12:00-14:00 GMT
d) scatter from colour sensor readings 12:00-14:00 GMT scatter from colour sensor readings 12:00-14:00 GMT

July 1994 date

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- Figure 6.31 Comparison of beam attenuation with the sum of the in situ derived absorption and scatter for the Pier Surveys
a) July Pier Survey 1994
	- a) July Pier Survey 1994
b) August Pier Survey 199
	- August Pier Survey 1995, using Spectron and Satlantic readings

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solid shapes use 0.33 b_b/a, open use Kirk

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solid shapes use 0.33 b_b/a, open use Kirk

Figure 6.32 Diffuse attenuation curves, averaged over survey
a) Satlantic measurements: Conwy 1996, Au

- Satlantic measurements: Conwy 1996, August Pier Survey 1995, Cwmystradllyn 1996 and Vestfjorden 1994
- b) UCNW Irradiance meter. Clyde 1994, Loch Striven 1994, Cardigan Bay 1994 and July Pier Survey 1994

c) UCNW Irradiance meter: Menai Strait Survey 1993-1994 monthly surveys

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7. LABORATORY RESULTS

7.1 SPECTRA

All absorption spectra decreased from the blue wavelengths to the red wavelengths, with water samples and yellow substance following an exponential decay, as did the furnaced filters. The average values for furnaced particles and yellow substance were very similar, with the errors overlapping. The exponents for all Menai Strait spectra, without the application of a pathlength correction, are shown in Appendix VIII, and are summarized in Table 7.1. Once a β correction of 2 has been applied to the furnaced particle spectra, the exponent is closer to that of the water sample.

Table 7.1 Exponents for spectra from the Menai Strait, regression of In values of zeroed spectra where r^2 >0.9

There was little variation in the cell water spectra throughout the year which suggests that the concentrations of the constituents in the cell were too low to show clearly, and the absorbance measured was a general background level, mainly due to yellow substance.

The 'fresh' filter spectra (and the dried filters) did not show an exponential curve as the mineral particles do (Fig. 7.1), indicating that the organic fraction dominates the

spectral shape of absorption.

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7.2 INTERCOMPARISON BETWEEN WATER PROPERTIES

To extract the signal due to a particular constituent the absorption curves can be regressed on the concentrations at each wavelength. This identifies the specific absorption curve for the constituent considered. This method is only valid where the constituents are totally independent of each other (Whitlock et al, 1982). The relationships between the concentrations in the Menai Strait are shown in Table 7.2.

Table 7.2 Correlation between constituents for the Menai Strait, omitting spurious values in May and June, and the Menai Pier Surveys

7.3 SPECIFIC SPECTRA

7.3.1 Phytoplankton

Fig. 7.2 shows the variation of the specific curve for JMB94, using the Cleveland & Weidemann (1993) correction and $\beta = 2$. This highlights the difference resulting from the method of correction. When the 'fresh' spectra are regressed on Chl concentrations (using $\beta = 2$) for June 1994, JMB94 and AMB95 (Fig. 7.3) the resultant spectra differ, showing that there is variation in the phytoplankton signal. However, all are in general agreement with Gallegos et al, 1990. AMB95 shows the least variation with wavelength as there was a limited range in pigment concentration over the survey to produce a clear signal in a regression. Both June and JMB94 have similar magnitudes to that in Gallegos et al (1990), but the "noise" in June, as a result of very low absorbance values, masks any clear signal. The JMB94 spectra are the clearest, and in good agreement with Gallegos et al. However, the red peak in this survey occurred at a lower wavelength (675 nm) than Gallegos et al, June and AMB95 (683 nm).

The 'constant' generated by these regressions follows an approximate exponential decay, in agreement with measurements taken of the dried filters, between 400 and 550 nm. At longer wavelengths the regression constant shows a peak characteristic of phytoplankton. This suggests that some pigments were not associated with the chlorophyll concentration in the regression, which is due to the similarity in the trend of the phytoplankton and inorganic concentrations. However, in general the dried filters gave an indication of the inorganic and detrital constituents (Fig. 7.4).

7.3.2 Mineral Solids

Similarly, regression can be used to calculate the specific absorption curve for MSS through the Menai Strait survey. Fig. 7.5 shows the curve calculated across the whole year, but when split into 'summer' and 'winter' the curves are slightly different,

with a more uniform spectrum occurring during the summer. This method of deriving

the specific spectrum through regression gives good agreement with the observed

spectra of the fumaced particles (Fig. 7.6). This confirms that furnacing the particles

at 500 °C does not change the optical properties of the minerals themselves (Bowers

et al, 1996).

The specific mineral spectra calculated from AMB95 are higher than those from the Menai Strait Survey, although the shape closely follows that from the summer months, as would be expected. The shape of the curves can most easily be compared by normalising all spectra to the value at 440 nm, this emphasizes the relative difference across the visible spectrum rather than the absolute magnitude. Such measurements of inorganic particles from Cardigan Bay and Cwmystradllyn are surprisingly similar to those in the Menai Strait with the error bars overlapping. However, the site-specific nature of this measurement is shown by comparing these spectra with that derived from the Conwy data (Fig. 7.7).

The constant from these regressions gives a curve of similar shape to that of specific chlorophyll, indicating that that the appropriate constituents had been identified (Fig. 7.8). The higher values at shorter wavelengths may represent a detrital component, forming an exponential curve upon which the pigments are superimposed.

7.4 ERROR DUE TO SCATTER

It is apparent that the pathlength amplification factor used on filters can greatly affect the magnitude of the calculated absorption spectrum. It therefore seems better to use spectra of suspensions. However, if particle concentrations are low there is an insufficient concentration within a 100 mm cell to produce a recognisable spectrum, as shown with the water spectra, whereas if concentrations are high, there is a possibility of particles settling while the spectrum is taken. In addition, there is scattering from the cell which is registered as loss due to absorption. This last problem can be improved by using an integrating sphere. Where this is not available the scattering component is reduced by placing a diffuser between the cell and the receiver, so that light scattered at low forward angles will be redirected towards the

sensor. This is not ideal as there will still be light scattered at greater angles, but it does produce a quantifiable reduction.

This technique was employed on kaolin samples (which are theoretically pure

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scatterers), and then on the second Conwy and Cwmystradllyn surveys. Increasing weights of kaolin were suspended in distilled water in the 100 mm cells and the spectrum taken, then a sheet (2 mm thickness) of white perspex inserted between the cell and the receiver and the spectrum re-taken, having shaken the cell to ensure the particles had not settled. The difference between the spectra (Fig. 7.9a), of the order of 50%, indicates the amount of scattered light which was redirected towards the sensor. Unfortunately, this cannot be converted into a percentage as the proportion

which is still scattered out of the cell is unknown.

This difference can equally be seen in the Conwy data (Fig. 7.9b), although the concentrations at Cwmystradllyn were too low to make any appreciable difference (and so are not shown). It is apparent that the diffuser makes a marked difference when there is a significant concentration of particles within the cell and therefore is a good method for gauging the scale of the scattering, even though it does not give the total value. In both the above cases, the contribution from forward scattering is independent of wavelength, confirming the work of Kullenberg (1968). The kaolin results imply that scattering at greater angles increases with decreasing wavelength as the remaining "absorbance" must be due to scatter at greater angles.

much work has been done on mineral reflection (e.g. Hunt, 1977; Hunt & Ashley, 1979; Hunt & Salisbury, 1976, Curran & Novo, 1988). However, the optical properties of glass have been defined, and the absorption curve which is derived from the optical attenuation follows an exponential curve with exponent -0.055. Glass is

However, when taking the kaolin spectra a mistake was initially made and the diffuser placed between the source and the cell, this gave very similar results at higher concentrations to those when the diffuser was in the correct position. This casts doubt on the effectiveness of the perspex, as when placed before the cell it should not have an appreciable effect, and there seems no apparent reason why the same results should be produced.

7.5 DISCUSSION

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The specific absorption curve for MSS has not previously been defined, even though

formed using quartz minerals, which are predominant in the Menai Strait. This value for glass suggests that the derived mineral spectrum is realistic as the observed exponent derived for minerals is also -0.055.

It has therefore been shown that the use of regression of the spectra from filter and solution measurements on the constituent concentrations can identify the specific absorption curves for each constituent. This method is only appropriate when the constituents themselves are independent *i.e.* the technique could not be used when

yellow substance was purely the derivative of phytoplankton. However, the only limitation in these datasets is the lack of variation in the different constituent concentrations for any particular survey, for example the small range of yellow substance throughout the Menai Strait Survey, and the lack of pigment variation in the August Pier Survey.

Even with these limitations it has been possible to classify each constituent optically, giving results which are compatible with those previously found in the literature, $e.g.$ Gallegos *et al* (1990) for phytoplankton and Tassan (1988) for yellow substance, and establishing a characterisitic spectrum for inorganic sediments.

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Specific chlorophyll spectra calculated with different pathlength Figure 7.2 amplification corrections, compared with Gallegos et al, 1990

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Figure 7.3 Specific chlorophyll spectra, calculated with $\beta = 2$, for June 1994, the Pier Surveys for July 1994 and August 1995

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Figure 7.4 "Constant" frum July regression, with average of dried particle spectra
a) values with standard error

- a) values with standard error
b) normalised at 440nm
- b) normalised at 440nm

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wavelength n_m

Figure 7.5 Specific inorganic spectra from Menai Pier Surveys. Filters are not zeroed, correction β =1.

Figure 7.6 Specific inorganic spectrum with average furnace spectrum for August normalised at 440nm. Filters are not zeroed.

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wavelength nm

wavelength nm

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Figure 7.7 Average of normalised spectra for various sites
a) furnaced spectra

- a) furnaced spectra

- b) dried spectra

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wavelength nm

Figure 7.9 Average of spectra with and without diffuser
a) kaolin a) kaolin
b) Conwy

Conwy survey

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8. COMPARISON BETWEEN LABORATORY AND FIELD MEASUREMENTS

In order to test the consistency of the measurements, the specific values for absorption and scattering derived from the *in situ* data can be compared with those measured in the laboratory. This comparison can be made in three ways: a) by comparing the derived absorption from the light sensor with the total absorption from the laboratory, and the derived scattering with the difference between the transmissometer attenuation

Kirk's (1985) algorithms for deriving a and b from R and K were tested with the field measurements in §6.6, when the beam attenuation coefficient from the transmissometer

and the laboratory absorption (§8.1); b) by relating the measured values of reflectance and diffuse attenuation with the ratio between b and a , calculated from the beam attenuation and the laboratory absorption (§8.2); c) by calculating the specific absorption values for each constituent from both the field and laboratory measurements and comparing these (§8.3 - the technique for regressing optical properties on concentrations to extract the specific values was described in §6.7).

was compared with the sum of a and b . As an alternative, the total laboratory absorption (the "fresh" filter spectra plus water and yellow substance) can be used as an independent value of absorption, and then subtracted from the transmissometer c to determine b , and hence test the derived values of a and b from the field separately. The use of Kirks algorithm (1994) for diffuse attenuation depends greatly on the influence of G. The value of G used was 0.256 as calculated for San Diego Bay. This is unrealistic for the Menai Strait which would have greater turbidity and therefore a lower value of G. It is also apparent that the value of G would change between the various sites visited. However, more suitable values of G were not

8.1 ABSORPTION AND SCATTERING

available and consequently this standard value was used. Kirk (1994) relates G to the solar altitude as well as the scattering phase function. In this respect, the values for the Menai Strait survey are unlikely to change as most surveys were undertaken with cloudy conditions and therefore a diffuse ambient light field, with little dependence on solar variation.

The comparison between absorption values for the July Pier Survey is shown in Fig. 8.1a-d - Fig. 8.1 a and b use β =2 correction on the particle spectra whereas, c and d use Cleveland & Weidemann (1993). The colour sensor values were calculated from the readings between 10:00 and 16:00; the extended time interval may explain the bias of the absorption to higher values relative to those in the laboratory as attenuation would be greater when the sun was lower. The values from the IRM1 are closer to the laboratory values; this was also observed with the field comparison as the profiles were taken at the same time as the water samples and the transmissometer readings. The difference between the methods of calculation, *i.e.* Kirk compared with $R=0.33b_b/a$, are small with respect to the scatter of points about a 1:1 line.

The scattering comparison can only be shown at 670 nm, the wavelength of the transmissometer (Fig. 8.2). The values calculated from the IRM1 readings show the same trend as (c-a) but are consistently too high (by -0.4 m^{-1}). In contrast, the colour sensor values are more scattered, but predominantly too low.

In the August Pier Survey, the values of reflectance from the Satlantic were considered dubious, and when using these, the scattering values were much lower than those estimated with the transmissometer (as shown in Fig. 5.24). In the field data, the combined absorption and scattering were in much better agreement with attenuation when using the Spectron reflectance. This improvement is also apparent with the scattering measurements (Fig. 8.3), those calculated from the Satlantic data alone being less than 3 m^1 , whereas (c-a) ranges from 4.5 to 8.5 m⁻¹. However, the absorption calculated from the Satlantic data shows good agreement with laboratory, whereas the Satlantic-Spectron values have a tendency to be too high, although in the correct range (Fig. 8.4a-d). This bias is most apparent when the Cleveland &

Weidemann (1993) correction is used (Fig. 8.4d). Once again, the difference when

using Kirk's algorithms is minor compared with the overall scatter.

8.2 b/a RELATIONSHIPS

A more direct test of Kirk's algorithms is to correlate R and K/a with b/a . Kirk (1994) relates these as:

$$
R = (0.975 - 0.629\mu_0) \frac{b_b}{a}
$$

where b_b = 0.019 b

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$$
\frac{K_d}{a} = \frac{1}{\mu_0} \left[1 + (0.425\mu_0 - 0.19) \frac{b}{a} \right]^{1/2}
$$

where K_d is the downward diffuse attenuation averaged over the euphotic zone

If μ_0 is assumed to equal 0.85 (Petzold, 1972), these become:

$$
R = 0.837 \frac{b}{a}
$$
 % *eqn. 8.1*

Fig. 8.5 shows the clear relationship between IRM1 R and b/a from observations during the July 1994 Pier Survey, producing a significant correlation:

$$
\left[\frac{K_d}{a}\right]^2 = 1.384 + 0.237\frac{b}{a}
$$

Reflectance and attenuation values were directly taken from sensor measurements, absorption was taken from the laboratory (as above), while scattering was calculated from transmissometer readings and is assumed constant over the visible wavelength range.

When forced through zero this becomes:

$$
R = 0.871 \frac{b}{a} + 0.985
$$

$$
r^2 = 0.725
$$

$$
p < 0.001
$$

$$
n = 30
$$

$$
R = 1.149 \frac{b}{a}
$$

If scattering is not considered constant with wavelength, the comparison can only be made for 670 nm:

$$
R = 0.411 \frac{b}{a} + 0.952 \qquad r^2 = 0.816 \qquad p < 0.001 \qquad n = 6
$$

which becomes

$$
R = 0.839 \frac{b}{a}
$$

This constant agrees well with that in equation 8.1.

In these equations the correlations should theoretically pass through zero, but the initial relationships fitted to the data have an intercept significantly different from zero, and therefore the zeroed relationship should not be used as a good fit.

It is apparent from Fig. 8.5 that the observations do not follow Kirk exactly, but have a greater gradient, although the values at 670 nm are similar.

The values for the August 1995 Pier Survey are shown in Fig. 8.6, using the reflectance from the Spectron. Three distinct relationships can be seen. The lowest relationship applies to only one day (23 August) and so has been considered invalid, as the low reflectance values may be due to shadowing effects. Most data points follow a relationship similar to that of Kirk, correlating as:

$$
R = 0.556 \frac{b}{a} - 0.092 \qquad \qquad r^2 = 0.736 \qquad p < 0.001 \qquad n = 36
$$

However, the values for 28-31 August follow a different relationship:

$$
R = 1.864 \frac{b}{a} - 2.015 \qquad r^2 = 0.759 \qquad p < 0.001 \qquad n = 18
$$

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For both these relationships the intercept is not significantly different from zero.

These three days cover the spring tide, where total suspended sediment concentrations were highest (max. 10.25 mgl⁻¹). This suggests that the relationship between b/a and reflectance may vary with the dominant source of reflectance. The greater slope is associated with the higher mineral concentrations and may indicate a higher backscatter ratio, consistent with the higher scattering contribution from harder

 $\sigma_{\rm{eff}}$, $\sigma_{\rm{eff}}$

Fig. 8.7 represents the $[K_d/a]^2$ to b/a relationship for the July Pier Survey. Fig. 8.7a uses the Cleveland & Weidemann (1993) correction for the absorption spectra, while Fig. 8.7b uses β =2. In both cases there is wide scatter. Similarly, Fig 8.8 a&b show the data for the August Pier Survey, excluding the points for 25 August due to their anomalously low values compared with the rest of the survey. The correlations for these are shown in Table 8.1. The equations for 670 nm only are included as this is the wavelength at which scattering was calculated. Although regression coefficients improve in the July data when only 670 is considered, the relationship is less significant (indicated by the higher p values) which suggests that scattering can be

considered constant over the visible range.

Table 8.1 Correlations between K_d/a and b/a for the Pier Surveys

All these graphs also show the relationship suggested by Kirk (1994), using $\mu_0 = 0.85$. For the JMB94 data the Kirk relationship is too low, and appears to delimit a lower boundary to the observed data. However, in the AMB95 survey the Kirk relationship is higher than the observations, though follows the same trend.

8.3 SPECIFIC SPECTRA

The laboratory values for phytoplankton pigment (described in §5.2.4) are within the

error bars of the instrument derived (Fig. 8.9), showing general agreement.

The IRM1 derived absorption values change slightly from winter to summer, the MSS absorption being slightly greater in winter (Fig. 8.10). This trend is not observed in the laboratory spectra, where the winter fumaced spectra appear to have a steeper exponential curve with less variation between the spectra, but are not greater in overall magnitude. The zeroed MSS spectra *(i.e.* the value at 750 nm was subtracted from all absorbances) were initially compared with the field data (Fig. 8.11) exhibiting a steeper exponential and lower values than observed in the field. However, if the spectra are not zeroed at 750 nm the more uniform absorption across the spectrum is in better agreement with the field data. This is most apparent when comparing the summer spectra with the IRM1 and those from AMB95 with the Satlantic data (Fig. 8.12). When all the Menai Strait values are combined the specific curve is lower than other measurements, but is the same shape as that derived from AMB95.

These spectra can be used to calculate a wavelength dependent value of β , by comparing the Menai Strait derived absorption with that measured in the laboratory. Initially, the *in situ* derived absorption was compared with β values of 2, 3 and 4 (Fig. 8.13), appearing to agree most closely with β =3. However, when the Satlantic data were used, $\beta = 3$ produced a curve which was too low at longer wavelengths. Conversely, $\beta = 2$ gave correct values at longer wavelengths but was too high in the

blue. Fig. 8.14 shows the higher absorption towards shorter wavelengths which may

be due to increased scatter that can be incorporated in β . When curves are fitted to

the observations, and the ratio calculated (Fig. 8.15), the resultant equation for β is:

β = 2.0 + 0.75 exp [-0.009 (λ -400)] eqn. 8.2

The successful comparison of these optical properties leads to the construction of the in situ readings from the laboratory measurements (Fig. 8.16-8.18), following the basic equations for total absorption in §2.3.1. These figures show the wet particles plus yellow substance and water for the Pier Surveys and the Clyde compared with the sensor absorption, while the Menai Strait comparison is the inorganic particle spectra, plus yellow substance, water and the chlorophyll concentration multiplied by the specific spectrum (corrected as per Cleveland & Weidemann, 1993) derived from the July Pier Survey. The series of three figures compares the corrections of Cleveland & Weidemann (1993), β =2 and β =(2+scattering) [*i.e.* equation 8.2]. The laboratory values match the *in situ* measurements best when the correction $\beta = (2 + \text{scattering})$ is used (Fig. 8.18), allowing for change across the spectrum. Fig. 8.19 uses the three methods of correction for the surface spectra and compares this with the *in situ* absorption. However, Fig. 8.20 uses the spectra for the middle sample, taken at approximately 3 optical depths. It is apparent that this sample gives better agreement with the instruments. This implies that optical measurements should be used with the average concentration throughout the euphotic zone and not just from surface

measurements, unless these are representative of the upper part of the column.

8.4 AVERAGE COSINE

The combination of the laboratory and field measurements can be used to determine the average cosine μ in the Menai Strait and how it varies throughout the year. This is calculated as the ratio between the laboratory absorption and the *in situ* diffuse attenuation. Fig. 8.21 shows the slight increase in all wavelengths into the summer, as the signal from the sun becomes stronger and higher in the sky. This is illustrated by the variation in the cosine receiver used with the IRM1 (Fig. 6.14).

8.5 SUMMARY

Within the different surveys, the variation due to the use of different reflectance equations appears minor in relation to the overall scatter. Consequently, this does not clarify whether the use of Kirk's (1985) algorithms is appropriate for these types of

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environment.

The comparison between the regression on the derived values from the *in situ* measurements and the regressions on the laboratory measurements are in good agreement when organic particles dominate *i.e.* in the summer months. However, the relationship between R and b/a may change with the nature of the particles, giving a steeper correlation when mineral particles dominate. It has been shown that the correction of mineral particles to zero at 750 nm is inappropriate, as there is a component of absorption as well as scattering in the spectrum measured in the infrared. An alternative pathlength amplification correction has also been suggested which is applicable to mineral particles with higher values of absorption than those previously calculated for phytoplankton. This correction was determined through the comparison of field and laboratory measurements and includes a wavelength dependency for scatter. When this correction is used, measurements from other surveys are in better agreement indicating that this correction is more applicable than the others used in this context.

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- Figure 8.1 Total laboratory absorption (water+yellow substance+fresh filter) compared with *in situ* absorption, for JMB94
a) colour sensor
	-
	- a) colour sensor
b) UCNW irradia
	- b) UCNW irradiance meter
c) colour sensor using C&V c) colour sensor using C&W (1993) filter correction
d) UCNW irradiance meter using C&W (1993) filter
	- UCNW irradiance meter using C&W (1993) filter correction

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Figure 8.2 Difference between transmissometer c and laboratory absorption compared with in situ scatter for JMB94, 670nm

Figure 8.3 Difference between transmissometer c and laboratory absorption compared with in situ scatter for AMB95, 670nm. The use of β =2 or C&W (1993) does not make an observable difference.

- Figure 8.4 Total laboratory absorption (water+yellow substance+fresh filter) compared with *in situ* absorption, for AMB95
a) Satlantic
	-
	- a) Satlantic
b) combined
	- b) combined Satlantic and Spectron
c) Satlantic with Cleveland & Weid Satlantic with Cleveland & Weidemann (1993) correction used for laboratory spectra
	- d) combined Satlantic and Spectron with Cleveland & Weidemann (1993) correction used for laboratory spectra

Figure 8.5 Irradiance meter reflectance compared with the ratio between scatter and absorption, where b=c-a, for JMB94

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Figure 8.6 Spectron reflectance compared with the ratio between scatter and

absorption, where b=c-a, for AMB95. Open symbols indicate data points which were omitted from the regression: 28-31 August 1995.

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 \mathbf{A}

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 $(K_d/a)^2$ compared with b/a, where K_d is from the colour sensor between Figure 8.7 09:00 and 15:00, for JMB94 (a=water+yellow substance+fresh filter)

- Cleveland & Weidemann (1993) absorption correction a)
- β =2 absorption correction $b)$

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 $\Delta \sim 1$ \sim

 b/a

 \sim

Figure 8.8 (K_d/a)² compared with b/a, where K_d is from the Satlantic, for AMB95 a) Cleveland and Weidemann (1993) pathlength amplification Cleveland and Weidemann (1993) pathlength amplification correction

 \mathbf{r}_c

 ~ 100 km s $^{-1}$

b) $\beta = 2$ correction

 \sim $\sigma_{\rm{max}}$ $\mathcal{L}=\mathcal{L}(\mathcal{L}^{\mathcal{L}})$. ~ 800 km s $^{-1}$ $\label{eq:2.1} \begin{array}{c} \mathcal{A} & \mathcal{A} & \mathcal{A} \\ \mathcal{A} & \mathcal{A} & \mathcal{A} \\ \mathcal{A} & \mathcal{A} & \mathcal{A} \end{array}$

 $\sim 80\%$ $\sim 10^{-10}$ km s $^{-1}$ **Contractor** $\ddot{\mathbf{r}}$

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Furnaced spectra for Menai Strait Survey 1993-1994. Filters not zeroed, Figure 8.10 $\beta = 2$

- average of all spectra $a)$
- average of winter spectra (Nov93-Mar94, Oct94) $b)$
- average of summer spectra (May94-Aug94) $c)$

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Sensor derived inorganic spectrum compared with fresh filter derived Figure 8.12 spectrum

> Satlantic $a)$

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Irradiance meter (summer) $b)$

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In situ inorganic absorption derived from Satlantic data compared with Figure 8.13 laboratory spectrum, derived from "fresh" filter spectra with β =2 and $\beta = 3$

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Comparison of smoothed laboratory derived spectrum (β =2) with in situ Figure 8.14 Satlantic spectrum from AMB95

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- 8.16 Comparison between total absorption calculated in the laboratory and in situ where filter spectra are corrected as Cleveland & Weidemann (1993)
a) Menai Strait Survey: furnaced spectrum + YS + water + Chl
	- a) Menai Strait Survey: furnaced spectrum + YS + water + Chl concentration multiplied by spectrum derived from JMB94
	- b) July Pier Survey: fresh filter spectrum + YS + water
c) August Pier Survey: fresh filter spectrum + YS + wa
	- c) August Pier Survey: fresh filter spectrum + YS + water

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- Figure 8.17 Comparison between total absorption calculated in the laboratory and in situ where filter spectra are corrected with $\beta = 2$
a) Menai Strait Survey: furnaced spectrum + Y
	- a) Menai Strait Survey: furnaced spectrum + YS + water + Chl concentration multiplied by spectrum derived from JMB94

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- b) July Pier Survey: fresh filter spectrum + YS + water
c) August Pier Survey: fresh filter spectrum + YS + wa
- c) August Pier Survey: fresh filter spectrum + YS + water

Values below the theoretical minimum for absorption are excluded from the regression.

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- Comparison between total absorption calculated in the laboratory and Figure 8.18 in situ where filter spectra are corrected with $\beta = 2 + 0.75 \exp[-0.009(\lambda - 440)]$
	- Menai Strait Survey: furnaced spectrum + YS + water + Chl a) concentration multiplied by spectrum derived from JMB94
	- July Pier Survey: fresh filter spectrum + YS + water $b)$
	- August Pier Survey: fresh filter spectrum + YS + water $\mathbf{c})$

Values below the theoretical minimum for absorption are excluded from the regression.

 $\mathcal{R}=\mathcal{Q}(\mathcal{C})$ $\mathbf{x} \in \mathbb{R}^{n \times n}$ $\label{eq:2.1} \frac{1}{\sqrt{2}}\sum_{i=1}^N\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2.$

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- Figure 8.19 Comparison between total absorption calculated in the laboratory and in situ for Clyde 1996 Survey: fresh filters + YS + water data from surface samples
a) filter spectra correct
	- a) filter spectra corrected as Cleveland & Weidemann (1993)
b) filter spectra corrected with $\beta = 2$
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b) filter spectra corrected with $\beta = 2$
c) filter spectra corrected with $\beta = 2$ filter spectra corrected with $\beta = 2+0.75 \exp[-0.009(\lambda - 440)]$

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- Figure 8.20 Comparison between total absorption calculated in the laboratory and in situ for Clyde 1996 Survey: fresh filters + YS + water data from mid-euphotic zone samples
a) filter spectra corrected as Cleve
	- a) filter spectra corrected as Cleveland & Weidemann (1993)
b) filter spectra corrected with $\beta = 2$
	- b) filter spectra corrected with $\beta = 2$
c) filter spectra corrected with $\beta = 2$
	- filter spectra corrected with $\beta = 2+0.75 \exp[-0.009(\lambda-440)]$

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Figure 8.21 Average cosine (a/K) calculated for Menai Strait Survey where absorption is total calculated in laboratory
a) filter spectra corrected as Cleveland a) filter spectra corrected as Cleveland & Weidemann (1993)
b) filter spectra corrected with $\beta = 2$

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b) filter spectra corrected with $\beta = 2$
c) filter spectra corrected with $\beta = 24$ filter spectra corrected with $\beta = 2+0.75 \exp[-0.009(\lambda -440)]$

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9. OCEAN COLOUR MODEL

Using the comparisons from laboratory and field work, a model was developed to predict diffuse attenuation and reflectance from the constituent concentrations. This was achieved by calculating the absorption and scattering for each substance, computing from these the total absorption, scattering and backscattering, and then substituting these values into the Kirk (1994) equations to calculate K_d and R. Initially, the model was based on yellow substance, phytoplankton and mineral

files - water absorption and scattering spectrum at 10 nm intervals Smith & Baker, 1981

particles, as these are the dominant contributors in the Menai Strait, however, detrital

particles were subsequently added, so that the model could be applied to other areas.

9.1 CALCULATION OF PROPERTIES

Inputs:

$a(x) = a_y(x) + a_y$.) + $a_c(\lambda)C + a_d(\lambda)CSS + a_m(\lambda)MSS$ where a is absorption coefficient, λ is wavelength, C is chlorophyll concentration, OSS is the organic detrital concentration and MSS is mineral suspended solids

The model requires two input files (pure water and phytoplankton) which cover the visible spectrum. It is possible to change these files to accommodate different phytoplankton curves.

The absorption curves for water and chlorophyll are contained within the input files, while yellow substance is assumed to follow (as Bricaud *et al*, 1981):

specific chlorophyll absorption at 10 nm intervals,

e.g. Gallegos et al, 1990

concentrations of chlorophyll, mineral and detrital suspended solids,

plus the absorption of yellow substance at 440 nm (g440)

9.1.1 Calculation of absorption coefficient:

It is assumed that the absorption terms are additive (Gordon et al, 1988):

concentration. Subscripts w, c, y, d and m are water, chlorophyll, yellow substance, detritus and minerals respectively.

$$
a_g(\lambda) = g440 \exp[-0.014 (\lambda - 440)]
$$

Detrital absorption follows the dried laboratory spectra, having removed the contribution from minerals. This gives an exponential curve:

 $a_a(\lambda) = 0.113 \, OSS + 0.012 \, OSS \exp[-0.015 (\lambda - 440)]$

Originally, mineral absorption followed the exponential curve from the laboratory. However, when the zeroed exponential spectra were used, the value in the blue was

much too high; consequently, the UCNW meter readings, which gave a wavelength independent absorption, were more appropriate. The constant used was derived by regressing the MSS concentrations on the absorption calculated from the meter readings. This gives:

 $a_d = 0.05$ MSS

Although this works well with the data from the Menai Strait Survey, other observations did give a slightly higher value in the blue, so that the model was adapted to include an exponential curve plus a uniform baseline for absorption, as derived from non-zeroed laboratory spectra and the Satlantic data:

 $a_m(\lambda) = 0.0205 MSS + 0.038 MSS \exp[-0.0055 (\lambda - 440)]$

In both particulate absorption curves, the constants and exponent can be altered to reflect local conditions as required. Thus wavelength independent mineral absorption can be substituted if appropriate.

9.1.2 Calculation of scattering and backscatter coefficients:

Scattering was initially divided into three components - water, chlorophyll and minerals. Values for water are contained in the input file from Smith and Baker (1982). Chlorophyll scattering followed Morel (1988):

$$
b_c = 0.12 \, \text{C}^{0.63}
$$
\nwhere b_c is the scattering coefficient for chlorophyll

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Mineral scattering was assumed to be dominated by MSS, employing a magnitude constant determined by Prieur & Sathyendranath (1981), and a wavelength dependency from Tassan (1994):

 $b(\lambda) = 0.42$ MSS (550/ λ)

These three factors were added to give total scattering.

backscatter ratio (b_b') . A constant value of 0.019 was used unless the chlorophyll concentration was less than 0.1 mgm⁻³ where a wavelength dependency was introduced (Gordon et al, 1988):

 $b'_b = 0.019(560/\lambda)$

Backscatter was then calculated by multiplying the total scattering coefficient by the

However, these relationships were empirically derived from various studies in different conditions, and were therefore deemed inflexible. Consequently, the scattering curves were then changed - Anomalous Diffraction Theory (Kirk, 1994) was used to calculate b for the phytoplankton, detrital and mineral particles. This is an approximation to

Mie Theory, and requires the density, refractive index and size of the particles. These parameters can all be interactively changed to local parameters, or default settings used if the nature of the particles is unknown.

The default values are based on values from the literature to give 'typical' characteristics of the particles. Thus, for phytoplankton the radius is $0.25 \mu m$, the density is 1.1 gcm³, and the refractive index 1.05 (Boney, 1975); for detrital particles, the radius is 2.5 μ m, the density is 1.2 gcm⁻³, and the refractive index 1.1; while for minerals, the radius is 1.5 μ m, the density is 2.2 gcm⁻³, and the refractive index 1.2. Table 9.1 shows the refractive index for different minerals.

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Table 9.1 Refractive indices for different minerals

The effect of using different radii is shown in Fig. 9.1. This figure illustrates the variation due to changes in the radius of mineral particles, while detrital particle, phytoplankton and yellow substance concentrations remain constant. This indicates the model's sensitivity to variation within the natural environment, as the radii observed will cover a wide range whereas only one value is used in the model. This will add significant error in the calculation of scatter due to the efficiency of the different particle sizes (Baker & Lavelle, 1984) as can be seen in the range of curves

As well as altering the calculation of b, the backscatter ratios were changed, so that each constituent is treated individually. Hence, 0.019 is still used for minerals, while

given in the figure. The variation due to radius is similar in the blue, green and red wavelengths, spanning a K_d range of approximately 4 m⁻¹ when MSS=50 mgl⁻¹. However, the combined effect with PAR increases the range of error, with a variation of 7.5 $m⁻¹$ caused at a concentration of 50 mgl⁻¹. The parameters of density and refractive index will also change, but these changes will be more marked between sites, or periods, where the nature of the particles changes, whereas size variation will be present at all times.

0.5 is used for water, 0.005 is used for phytoplankton and 0.01 is used for organic

detritus. These values allow for the variation in the refractive index between the

particles, and their absorption properties; they may all be changed by the user.

Backscattering is then considered additive to give the total value.

9.1.3 Reflection and Attenuation

The above coefficients may then be entered into equations suggested by Kirk (1981) to calculate R and Kd:

$$
R(\lambda) = (0.975 - 0.629\mu_0) \frac{b_b(\lambda)}{a(\lambda)}
$$

$$
Kd(\lambda) = \frac{a(\lambda)}{n} [1 + (0.425\mu_0 - 0.19) \frac{b(\lambda)}{a(\lambda)}]^{1/2}
$$

μ_{0} where μ_0 is the average cosine

Although the average cosine is given a default value of 0.85, it can be changed to describe the specific light field more closely.

Alternatively, the basic reflectance equation can be used:

$$
R(\lambda) = 0.33 \frac{b_b(\lambda)}{a(\lambda)}
$$

9.2 MODEL MODES

The model is designed to be used for three main purposes:

- i) to observe how the attenuation and reflectance change as the constituent concentrations change
- ii) to give attenuation and reflectance curves for known concentrations
- iii) to show and output to a file the predicted attenuation and reflectance values for a large dataset of concentrations

Therefore the model has three "modes" of operation.

The first screen asks the user whether they want to change the settings for calculating the optical characteristics. If yes, the model shows the names of the files used to input the chlorophyll and water values, plus the various equations used in the model, listing the constants within these, and the default values. These can then be

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interactively changed. After these, the equations for reflectance and attenuation are shown, with an option to choose either the basic reflectance equation or that from Kirk (1994). Finally, the settings for the axes of the screen graphs are given and can be changed for unusually clear or turbid waters.

Once set, another menu is given, to choose the "mode" required.

Mode 1

Each constituent can be chosen to increase or decrease by a set amount so that

the reflectance curves can be seen as a constituent concentration changes. This can occur while the other constituents remain at zero, or at higher values. Mode 2

- colout.abs total absorption
- colout.sct total scattering
- colout. att diffuse attenuation
- colout. ref $-$ reflectance as $%$
- colout. bma beam attenuation

A particular value is input for each constituent, so that a combination of concentrations can be observed. This is designed to study cases of specific interest. The results can be printed to five files. The user inputs the stem of the filename, and extensions are added: abs, sct, bma, att and ref.

Mode 3

An input file is required with the constituent concentrations; this should have header line for general information, then the number of sites on the next line.

Subsequent lines should have the MSS, OSS, Chl and g440 concentrations separated by spaces. The optical properties are printed to five files (if wanted), all of which contain the concentrations, and then:

The output data can be printed at 10 nm intervals, or at ten wavelengths:

410 440 490 510 520 550 570 600 670 700

which cover most optical sensor wavebands.

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9.3 APPLICABILITY OF THE MODEL

To test the model the concentrations from all surveys were used, excluding those where there was doubt about the accuracy of the measurement. The model predictions have not been compared with laboratory measurements, as these were the basis for the model.

The scattering values, although following the same trend have a high degree of error (Fig. 9.4). This error is compounded in the reflectance values (Fig. 9.5), producing a wide region of scatter with an upper limit to the model predictions. This upper limit is governed by the b_h : a ratio for mineral solids. The higher reflectance values are mainly due to mineral solids, so the b_b : a ratio is dominated by the minerals, and thus

Fig. 9.2 shows the comparison between in situ derived absorption and the model, using default values. The predictions are close for all wavelengths although there is

a tendency to overestimate absorption, and at two points from the Conwy estuary the model predicts very high values due to high concentrations, which are not apparent in the optical observations. The same pattern is observed in the diffuse attenuation values (Fig. 9.3).

reflectance, which is proportional to this ratio. Consequently, the model will always reach a limit above which it will not predict, although the value of this will change with the nature of the particles. Such a limit in reflectance has been observed by Curran & Novo (1988), although the measurements in the Menai Strait exceed this predicted limit. High reflectance values would be expected in lakes which have very fine, white particles (such as glacial flour, as observed in Lake Tekapo, New Zealand, where the PAR reflectance can exceed 35%, Davies-Colley pers. comm.) where the particles would have a very high scattering coefficient and very low absorbance. Values in the Menai Strait would be expected to be much lower than this due to the organic fraction of particles and the type of sediment in the area.

It was only possible to compare beam attenuation predictions for the Pier Surveys (Fig. 9.6). The higher values are from AMIB95 while the cluster at lower values is from JMB94. The uniformity in the model results shows the effect of increasing

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phytoplankton with decreasing minerals so maintaining an approximately constant level of $a+b$ whereas the observations of c mirror the trend in minerals. This suggests that the minerals dominate the attenuation signal in this survey. Once again, the degree of error could be attributed to the variability of the scatter.

The error in the scattering prediction is thought to be due to the use of default values for the particle characteristics, as the particles would change throughout the year and would be a mixture of different types. However, although a particle analysis was

undertaken twice to study the particle characteristics (Appendix IX), the instrument was not available for most of the surveys, so that the accuracy of these parameters cannot be improved. The resolution for the size measurements only extended to $2 \mu m$ which did not cover the range necessary for the model input. There is a peak of smaller particles below this diameter which sugget that the model estimates of 1.5 μ_0 are realistic. It was originally intended that a parameter for particle size distribution could be incorporated within the model, and so use these measurements further. However, this development was not possible within the time constraints of the work although would be an interesting development for future modifications.

The effect of increasing each constituent separately is shown in Fig. 9.7 a-d. The reflectance of water alone shows the clear blue spectrum expected. An increase in chlorophyll produces a gradual change from blue to green, as is observed in a phytoplankton bloom, while pivoting around the value at 505 nm as previously observed (Bukata et al, 1983). The yellow substance decreases the level of reflectance, while the spectrum becomes more uniform; this agrees with observations of lakes with high humic concentrations which appear almost black due to the high absorption. Conversely, the minerals increase the reflectance, particularly in the red which gives the water a bright brown appearance, as observed in the Conwy estuary (Fig. 9.8).

To extend the usefulness of the model to more general ecological studies, the value for PAR diffuse attenuation and reflectance have been added. These can be used for light limit levels, used in plant species studies in freshwater lakes, where the \bullet \bullet

succession is dependent on the level of PAR reaching the bed (Schwarz, pers. comm.).

A listing of the model is given in Appendix X.

9.4 MODEL INVERSION

The ultimate aim in many such studies is to invert the model in order to estimate the concentrations from the optical signal. The model indicates that reflectance can vary

The use of absorption for an inverse model restricts its applicability to in situ observations where absorption can be measured, or calculated. The equation for total absorption has four variables (the concentrations) assuming that the specific absorption

greatly with relatively minor changes in the particle characteristics. It is therefore better to use inherent optical properties which are directly related to the particles, to estimate the concentrations. Scattering can also change greatly with variations in the particulates rather than the concentrations. Thus, the most effective method is to use the absorption. Although variable, in coastal waters with varying concentrations of constituents this is the most consistent optical property.

coefficients are known. Therefore, with in situ measurements at four or more wavelengths the concentrations can be calculated, as the unknowns are overdetermined. The most efficient method of calculation would be through matrices. However, for ease of determination, simultaneous equations can also be used, and are more flexible if the number of channels (or equations) are not known in advance. Consequently, a second program was written to obtain the concentrations from the absorption coefficients, using the specific coefficients given in Table 9.2.

This inversion is limited by the use of the specific absorption values, which may be incorrect for the particular location. However, Fig. 9.9 shows the concentrations of

mineral solids extracted from the absorption values for the Menai Strait. Although

scattered, the concentrations give an approximation to the conditions within the water.

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Table 9.2 An example of specific absorption values for each constituent at five wavelengths as used in the model. Sources: water (Smith & Baker 1983), yellow substance (Tassan, 1988), phytoplankton (Gallegos et al, 1990) and mineral solids from observations

For an independent test, absorption values from Palmer (1985) were used in the model, giving a better result for the mineral concentrations predicted (Fig. 9.10). However, although these were able to estimate the inorganic concentrations the values

for chlorophyll and yellow substance were very inaccurate (Table 9.3), which suggests that only the dominant concentration can be estimated with any confidence.

9.5 SUMMARY

The predictive model uses semi-analytical techniques to predict inherent and apparent optical properties from constituent concentrations. The equations used within this are defined but each constant can be changed as appropriate to any particular location. When using the default values derived from observations in the Menai Strait, it seems possible to predict absorption and diffuse attenuation closely, but the error involved in the scatter predictions becomes more marked in the reflectance signal giving a poor

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fit for both these parameters.

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- Figure 9.1 Diffuse attenuation calculated by the model for different radii of inorganic particles
a) 440 nm
	-
	- a) 440 nm
b) 550 nm b) 550 nm
c) 670 nm
	- c) 670 nm
	-

d) PAR

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Figure 9.2 Model absorption compared with observed absorption for all surveys (a) 440 nm

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- a) 440 nm
b) 490-520 b) 490-520 nm
c) 550-570 nm
- c) 550-570 nm
d) 670 nm
- d) 670 nm

Anomalous values and those below the theoretical minimum are excluded from the regression.

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- Figure 9.3 Model diffuse attenuation compared with observed attenuation for all
	- surveys
a) 4 a) 440 nm
b) 490-520
	-
	- b) 490-520 nm
c) 550-570 nm c) 550-570 nm
d) 670 nm
	- d) 670 nm

Anomalous values and those below the theoretical minimum are excluded from the regression.

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Figure 9.4 Model scatter compared with observed scatter for all surveys
a) 440 nm

-
- a) 440 nm
b) 490-520
- b) 490-520 nm
c) 550-570 nm c) 550-570 nm
d) 670 nm
- d) 670 nm

Anomalous values and those below the theoretical minimum are excluded from the regression.

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Figure 9.5 Model reflectance compared with observed reflectance for all surveys a) 440 nm

-
- a) 440 nm
b) 490-520
- b) 490-520 nm
c) 550-570 nm c) 550-570 nm
d) 670 nm
- d) 670 nm

Anomalous values and those below the theoretical minimum are

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excluded from the regression.

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Figure 9.7 Model reflectance for different constituents
a) pure water

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a) pure water
b) increasing b) increasing chlorophyll concentration
c) increasing yellow substance

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- c) increasing yellow substance
d) increasing inorganic particle increasing inorganic particle concentration

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Figure 9.8 Conwy estuary at Dolgarrog

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Figure 9.9 Inversion model compared with measurements of mineral substances in the Menai Strait Survey

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Figure 9.10 Inversion model compared with measurements of mineral substances in a Menai Strait Survey by Palmer 1985

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10. DISCUSSION

Observations at different sites over time have highlighted that the optical characteristics of the water constituents change spatially and temporally. Although models can be constructed from general observations, which are then useful in approximating the overall optical properties, it is necessary to know local conditions for a more detailed and accurate prediction (Ivanov & Kumeysha, 1993). Other studies have tried to distinguish different species of phytoplankton from the optical

The observed values in the Menai Strait for diffuse attenuation and reflectance are in good agreement with other studies which range from 0.06 m⁻¹ to 2.9 m⁻¹ for K_d in nonestuarine, coastal waters (Kirk, 1994). The absorption values measured in the laboratory and derived from the in situ measurements are comparable to spectra observed by others for yellow substance (e.g. Bricaud et al, 1981) and phytoplankton (Gallegos et al, 1990). The observed values for K_d and R covered a greater range than those measured in the equivalent study by Weidemann & Bannister (1986) who found ranges of 0.8-1.2 m⁻¹ and 3-6% respectively. They also derived absorption and scattering from these values to give ranges of 0.44 -0.83 m⁻¹ for absorption and 1.8-5.0 m⁻¹ for scattering - smaller ranges than in the Menai Strait but of a comparable

signal and have demonstrated that species and stage of development have a significant effect on the 'colour' of the water. However, it is also necessary to consider any changes in the yellow substance and mineral particles, particularly in Case 2 waters. As the geology changes with site so will the dominant particles within the water. For surface studies in relatively deep coastal water, the size and density of the mineral particles will be limited, as they remain in suspension and must therefore have a low settling velocity. However, in water bodies where there is a high degree of mixing and resuspension, such as estuaries, the particle composition can be much more varied, and thus the interpretation must encompass this.

magnitude. That study also found an independent estimate of absorption to be in reasonable agreement with the derivation through the Kirk (1985) algorithms.

The other sites used in this study were mainly to provide a contrast to test the model

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which was developed. However, the reflectance spectra from Llyn Cwmystradllyn agree well with the Type 3 lake discussed by Vertucci & Likens (1989) although they do not comment on the general environmental implications of the colour.

There were several possible sources of error within both the field and laboratory measurements. It was unfortunate, but unavoidable, that different instruments were used throughout the survey so that consistency could not be maintained. Although the various instruments were compared, the problems of particular sensors failing to

download, or other malfunctions, led to ambiguity within the comparisons.

The in situ measurements of K_d were limited with the UCNW instruments by the amount of time necessary to measure the light level at each depth. This also affected the reflectance measurements, although there were further errors in this property due to self-shading for the K_u values used to calculate R and the time lag between upwelling and downwelling observations. With the PRR-600 and the Satlantic, reflectance was affected by the conversion used to calculate upwelling irradiance from the radiance value. This indicates that the diffuse attenuation results were more robust and should be given more import in the analysis. There was thus greater confidence

in this parameter when constructing the model. Even though the observations of K_d are acceptable, the lack of incorporating the influence of the volume scattering function through using a variable G (as discussed in §2.4.2) will increase the error in the derivation of a and b.

The concentration measurements were limited by the lack of replicates taken during the Menai Strait Survey, making it difficult to determine the precision. In later studies the pigment concentrations are consistent within 10% (Appendix VII). Yellow substance measurements in relatively stable environments are consistent to 0.01 m^1 -1% of the total absorption. However, in dynamic environments such as the Conwy

Estuary on the flood-tide this error increases to 10%. The sediment concentrations, when three replicates were taken agree to within 0.1 mgl⁻¹ for the filters without a blank beneath, when the total concentrations were of the order of 20 mgl⁻¹. The third filter (used with a blank) consistently had a higher concentration which suggests that

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the error was increased by this technique. For non-blank measurements, this implies that the error was of the order of 1% .

In the laboratory, the main source of error was due to scattering as discussed in §7.4. This is particularly important with the inorganic particles where scatter dominates the optical signal and may alter with wavelength, as is suggested through the measurements using a diffuser. Given the uncertainties within the optical properties of the sediment it is difficult to distinguish between the absorption and scattering contribution. This is particularly important when determining the best value for the pathlength amplification factor. Although studies have been undertaken to calculate the best β for phytoplankton studies, there has been little work including inorganic particles. Thus, it was necessary to derive a new value for β from the in situ and laboratory measurements, which improves comparisons in this study and suggests that more work should be done to investigate this variable.

The mability to measure scatter accurately in the laboratory led to limitations in modelling this parameter within the final model, resulting in high variation with the scatter coefficients derived.

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For future studies which investigate the links between the apparent and inherent optical properties with an aim to predict the colour from the constituent concentrations, it is most important to take more accurate measurements of the particle concentrations, through the use of more replication and greater volumes of water. This is logistically difficult but would improve the confidence that can be given to the final results. In addition, the optical measurements should be replicated so that several profiles are done at any one time to ensure that brief fluctuations are not incorporated when they may have no relation to the water samples taken.

The comparison between inherent and apparent properties will only be truly achievable when in situ measurements of absorption and scattering can be taken. The development of such absorption-scatter meters is now occurring and should be used to understand the links between these properties as it is the inherent optical properties which will lead to more accurate predictions of concentrations.

At present, the model can only reproduce observed conditions where the parameters are specified for each site. This suggests that any inverse model, which estimates concentrations from the optical signals will also be site specific, and should incorporate as much local information as possible. Without detailed information, about the minerals in particular, the ability to distinguish the constituent signals from the optics is limited. Further information may be gained by extending the

measurements beyond the visible part of the spectrum, as it may be possible to quantify mineral concentrations in the infrared portion of the spectrum, or use redinfrared ratios for phytoplankton (Quibell, 1991; Han et al, 1994). However, these techniques need further investigation.

Satellite algorithms are particularly restricted, as the only information available is the upwelling radiance, which limits interpretation to the reflectance signal alone. For example, the upward radiance in the blue may be dominated by yellow substance fluorescence (Spitzer & Dirks, 1985) which would increase the signal above that expected with the concentrations present. The image may also be influenced by

surface foam, and wind roughening (Tassan, 1994) which increase the level of the signal, plus other scattering effects at the air-sea interface (Carter & Duncan, 1993), and atmospheric effects (Viollier et al, 1980). Remote optical sensors are therefore more useful in conjunction with other types of images, *i.e.* those from fluorescence sensors (Gower & Borstad, 1981; Mitchell & Kiefer, 1988a) or infra-red sensors (Stramska & Dickey, 1993). Combined images can then be used to locate areas of pollution (Clark, 1993; King et al, 1993), and algal blooms with association to physical structure (Mitchelson, 1984).

It may be possible to employ remote sensors in monitoring physical features which

are strongly linked to optically prominant constituents. For example, yellow substance appears to be conservative and gives a good correlation with salinity in the River Clyde. However, the extent of this correlation is surprising given that the source of the yellow substance will change when beyond the river itself. In the deeper water

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of the Clyde Sea, the expected source would be phytoplankton detritus rather than terrestrial humic acids, and consequently there seems no logical reason why the inverse relationship with salinity should be maintained. In a closed system with a terrestrial source, the change in salinity is due to dilution of fresh water with salt water, so that the optical signal becomes a reliable indicator of salinity. This relationship is dependent on the signature of the humic acids remaining constant and identifiable for the specific location. The use of yellow substance as a tracer is most appropriate for estuaries, which are, unfortunately, the most complex areas for distinguishing the different optical signals, usually bearing high phytoplankton and mineral loads, and thus complicating the determination of the yellow substance concentration from the colour.

Inherent optical properties are more accurate for monitoring constituents as they are directly linked to the constituents themselves. This necessitates in situ monitoring, and is thus suitable for buoy deployments over time. However, the validity of buoy measurements is dependent on the rate of fouling. Estimates of the constituent concentrations will improve with the amount of information available, so that if absorption and scattering can be measured the estimates will be more accurate. This can be achieved by using a transmissometer in conjunction with a nephelometer, or an absorption-scattering meter if available. The accuracy would be improved with additional information about the nature of the particles, such as particle size analysis from acoustic backscatter (Lynch et al, 1994). When only general radiance/irradiance meters are used the error is increased as the inherent properties must then be derived from reflectance and attenuation, and the relationships between these can be dependent on local conditions. As shown, the scattering depends on the nature of the particle and the total cross-sectional area (Owen, 1973), but it also varies with the light intensity, and can be more dependent on this than an increase in concentration (Ackleson et al, 1993). This emphasizes the importance of several types of sensor

being used together.

Further studies on the relationships between the optical properties and the constituents

may improve the accuracy of predictions and enable models to be used more widely.

However, it is also important to consider the effect of the laboratory techniques upon the results within any particular study. The use of spectra is particularly sensitive as the temperature of the water blank compared with the sample is important (Pegau & Zaneveld, 1993), the subtraction of the value at 750 nm is widely used and may not be applicable, particularly in studying mineral particles. In addition, the correction for the pathlength amplification factor is highly variable. There is also error added by using the absorbance measured with a spectrophotmeter as proportional to absorption, given that scattering of particles in cells and on filters may make a significant contribution. Even the use of an integrating sphere or diffuser system will not eradicate scattering completely. Consequently, there must always be a margin of error accepted within such results; although not perfect these methods are the most effective that can be widely employed.

It is debatable whether more extensive studies at a greater number of sites would produce algorithms for global use. Optical models are useful in identifying the dominant constituent within the water column, and the presence of other substances, but may not achieve precise concentrations with the instruments and knowledge available at present. In shallow water, the use of optical sensors may be a good method for relatively rapid coverage of bed composition, giving an indication of the sediment type and degree of vegetation cover. Limitations will occur from the field of view of the sensor, particularly in areas of highly diverse coverage, and identification of individual species, but may still be useful for monitoring gross change.

In general, optics can be used as a relatively cheap and simple method of monitoring over wide areas, with remote sensing, or over long time periods, with buoy deployment. It is not yet possible to use such data to estimate concentrations or species of phytoplankton accurately but the information is useful to gauge the general

condition and any change which occurs. Further studies in the more optically complex areas such as estuaries and Case 2 waters will enhance the knowledge and understanding of optical characteristics and may hopefully extend optical use to more precise applications.

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Optical Models in the Literature

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comments

- spectral albedo interpreted by optimization investigates inversion for scattering backscattered radiation field included fluorescence inverse model 928889888999
- irradiance can be estimated with abs & vol scat function only vector irradiance generated by isotropic source Raman scattering & fluorescence
	- inverse model with CZCS iterative inversion
		-
- mean concentration determines E(0) not vertical distribution YS & inorganic spectra similar covariation of concentrations five component model
- determines Chl, MSS & YS from diffusely scattered radiation two refl ratios used to estimate Chl

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Examples of models

Empirical

comparison of seven models reviews four types of model

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Monte Carlo

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Jonasz & Prandke Gordon & Brown Morel & Bricaud **Wilson & Kiefer**

Vasil'kov & Kopelevich **Bricaud & Morel** Gordon et al Plass et al Koepke

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Reviews

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Definitions of

Basic Optical Properties

BASIC DEFINITIONS

To consider the physics and interacting processes within a light field, it is necessary to define the standard concepts and properties.

Visible radiation from the sun is divided into quanta of energy, known as photons; the time rate of flow of this radiant energy is termed the radiant flux (Φ) . The strength of this energy is measured as the radiant intensity (I) - "the radiant flux

emitted by a point source, or by an element of an extended source, in an infinitesimal

where Φ is radiant flux, θ is the zenith angle, ϕ is the azimuth angle, ω is the solid angle and A is area

cone containing the given direction, divided by that element of solid angle" :

$$
I = \frac{d\Phi}{d\omega}
$$

The most commonly studied parameters of the underwater light field are radiance and irradiance

radiance is "the radiant flux per unit solid angle per unit projected area of a surface":

while irradiance is "the radiant flux incident on an infinitesimal element of surface containing the point under consideration, divided by the area of that element" (Jerlov, 1968):

$$
E = \frac{d\Phi}{dA}
$$

Energy which enters the water from above and is transmitted downwards is known

as *downward irradiance*, while photons which travel upwards, having been diverted

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from their downward path, produce upward irradiance.

Scalar irradiance E_0 is the integral of the radiance distribution at a point over all directions about the point. The ratio of the net downward irradiance to scalar irradiance is known as the average cosine:

The ratio between the reflected and the incident radiant flux is termed the reflectance, a special case of which is the *irradiance ratio*, the ratio most often

$$
\bar{\mu} = \frac{E_d - E_u}{E_0}
$$

referred to:

$$
R = \frac{E_u}{E_d}
$$

The vertical gradient of the logarithm (natural) of radiance, or irradiance, is known as the vertical attenuation coefficient:

$$
K = -\frac{d \ln(X)}{dz} = -\frac{1}{X}\frac{dX}{dz}
$$

where X can be either radiance or irradiance and Z is depth

The directional nature of the radiant energy is determined by the volume scattering function $[\beta(\theta)]$ - "the radiant intensity, from a volume element in a given direction, per unit of irradiance on the cross-section of the volume and per unit volume (V)":

$$
\beta(\theta) = \frac{dI(\theta)}{EdV}
$$

The change in radiance over a certain length consists of loss by attenuation (c) and gain by scattering (Jerlov, 1968):

$$
\frac{dL(z,\theta,\phi)}{dr} = -cL(z,\theta,\phi) + L^*(z,\theta,\phi)
$$

where L is radiance, r is distance between source and receiving point, c is the beam attenuation coefficient, θ is angle from the zenith, and ϕ is azimuth angle

The latter term $[L^*(z, \theta, \phi)]$ is known as the path function, being the double integral of the product of the radiance and the volume scattering function; it decreases with depth at the rate of the diffuse attenuation coefficient:

For an optically uniform medium this can be integrated along (z, θ, ϕ, r) to give the apparent radiance:

$$
L^*(z,\theta,\phi) = \int\limits_{\phi'=0}^{2\pi} \int\limits_{\theta'=0}^{\pi} \beta(\theta,\phi;\theta',\phi') L(z,\theta',\phi') \sin \theta' d\theta' d\phi'
$$

$$
L^*(z,\theta,\phi) = L_0(z_t,\theta,\phi) e^{-\sigma} + \int_0^r L^*(z',\theta,\phi) e^{-c(r+\theta)} dr
$$

which becomes:

$$
L_r(z,\theta,\phi) = L_0(z_t,\theta,\phi) e^{-\sigma} + \frac{L^*(z,\theta,\phi)}{c + K\cos\theta} (1 - e^{-(c + K\cos\theta)r})
$$

For a path directed at zenith, this gives:

$$
L(z) = L_0 e^{-cz} + \frac{L^*(z)}{c-K} (1 - e^{-(c-K)z})
$$

= $L_0 e^{-cz} + \frac{L^*(0) e^{-kz}}{c-K} (1 - e^{-(c-K)z})$

As depth increases below the surface, the amount of light present decreases. This decrease can be quantified as the ratio of the radiant flux lost from a beam to the incident flux, which is known as *attenuance*. If the attenuating processes are uniform in all directions, the <u>rate</u> of decrease of upward irradiance is equal to that of downward irradiance, although at a lower level of energy. This 'loss' is due to both absorption, where photons are effectively extinguished, and scattering, where the

photon is redirected. It is generally accepted that attenuation is due only to these two processes, and that they are additive, so that the attenuation coefficient can be

defined as the internal attenuance of a infinitesimally thin layer of the medium normal

to the beam, divided by the thickness of the layer (Δr) :
$$
c = \frac{-\Delta \Phi_c / \Phi_b}{\Delta r} = a + b
$$

where a is the absorption coefficient and b is the scattering coefficient, both in $m⁻¹$.

while absorptance is the ratio of the radiant flux lost from a beam by means of absorption (Φ_a), to the incident flux (Φ_a).

The absorption coefficient (a) is defined as the absorptance (A) of an infinitesimally thin layer of the medium normal to the beam, divided by the thickness of the layer (r),

$$
a = -\frac{\Delta A}{\Delta r}
$$

$$
A = \frac{\Phi_a}{\Phi_o}
$$

Scatterance (B) is the radiant flux scattered from a beam (Φ_b) , to the incident flux:

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Thus, the total scattering coefficient (b) if the scatterance of an infinitesimally thin layer of the medium normal to the beam, divided by the thickness of the layer.

$$
b = \frac{\Delta B}{\Delta r}
$$

Preisendorfer (1959) categorized optical properties as either apparent or inherent. Apparent properties are those which are affected by changes in the radiance distribution, while inherent properties are independent of this. Thus, attenuation, absorption and scattering coefficients are all inherent properties, as is the volume scattering function, as they are not affected by the direction of the light nor its intensity, while radiance and irradiance are apparent.

The refractive index is "the phase velocity of radiant energy in free space divided by the phase velocity of the same energy in a specified medium".

All definitions are taken from Jerlov (1968), and Morel and Smith (1982).

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IRM 1 Calibration Curves

Response curves for each channel + diffuser effect

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Response curves compensated for the effect of the diffuser

Normalised response curves to allow comparison of half-band widths

wavelength nm

APPENDIX IV

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Comparison of Spectron Data

taken With and Without a Pipe

Comparison of Yellow Substance

Measurements using a Membrane Filter

or a GF/F Filter

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These measurements were taken on water samples from the Conwy River

APPENDIX VI

Comparison of Spectra

with Filter over Spectrophotometer

Source or Receptor

wavelength nm

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APPENDIX VII

Raw Data

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Menai Strait: Constituent Concentrations Diffuse attenuation and Reflectance

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Other Sites: Constituent Concentrations Diffuse attenuation and Reflectance

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APPENDIX VIII

Exponents of Spectra from

Menai Strait Survey

Filter Spectra:

All particles

Inorganics

Cell Spectra

Water samples

Yellow Substance

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VOLUME DISTRIBUTION TABLE (PERCENT)

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PROBABILITY VOLUME DENSITY GRAPH

Name: HENAI SIRAIT G1 $3.5E-85$ cc/nl(189.8 %) Mean(nv): 5.83 Pm $S.D.$ (nv): 2.63 *yn* Mode at 5.83 pm ((SCALE RANGE (yn): ADJUSTED)) $\langle \rangle$. $7.87 -$

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CELL TYPE : LQFLOW : SAMPLE SIZE : 4
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VOLUME DISTRIBUTION TABLE (PERCENT)

SAMPLE NAME : MENAI STRAIT G2

FILE NAME : Data Not Saved.

 $\mathsf{p} \star \mathsf{r} \mathsf{c}$ DATE : $-24/021$ 24/03/19 \overline{a} ACQ. $-0.11C$ RANGE :
HAAF 2.600 2-600
-**COLINT** COUNTS :
COUNTS -250205 358295 TIME . 15: 06 ACQ. MODE : SAMPLE S. N. F. : 0.82 CONFIG. : 2 (0.5 A) ; ACQ. TIME : 930 SEC ; S.D.U. : 589
es:: wes : leflou CELL TYPE : LQFLOW | SAMPLE SIZE : 5 (ABORTED) | CONCENTR.: 2.0E+05 #/ml SAMPLE TYPE : SPECIAL /L; REQ. CONF. : None ; SOLIDS : 2.2E-03 %

UNDER(cc/ml) SIZE (microns) OVER(cc/ml)

1.120E-06 3.29 2.128E-05

b

16

16

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 ϵ **Contract Contract Contract**

HUMBER DISTRIBUTION TABLE (RANGES)

SAMPLE NAME : MENAI STRAIT G2

FILE NAME : GMS2. DAT

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Computerized Inspection System

SAMPLE NAME : MENAI STRAIT G2 FILE NAME : Data Not Saved.

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σ τ σ σ σ GALAI Computerized Inspection System

PROBABILITY UOLUME DENSITY GRAPH

Name: MSIRAITI $9.32 - 36$ cc/n1(189.8%) $Hean(w)$: 6.44 un Hode at 77.89 pm $S.D.$ (nv): $3.13m$ $3.8% -$

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Median : 28.18pm Mean(vm): 31.63pm S.D. (wa): 28.41pm $Comf(v_n)$: 95.33 χ

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Size (in sicrems)

G A L A I - C I S 1 O O O

Computerized Inspection System

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UCNW Particle Shape Analysis

```
SAMPLE NAME : cbtest4
FILE NAME : MSTRAIT1
```


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 $\mathcal{L}_{\mathcal{F}}$

APPENDIX X

Listing of

Ocean Colour Model

'colallss - colour model modified 11/95 to include mss higher abs ********** 'also 19/01/96 to use Mie scat for chl: needs chlcoef.dat for input ********* '20/07/96 includes detrital absn as well as MSS ****************************

'24/09/96 calcs PAR attenuation and reflectance *******************************

'calcs scat by anomalous diffractive theory (kirk p90) ***********************

```
andinput - interactive creation of input file for colour model
```

```
DECLARE SUB inposprn (xpt!, ypt!, txt$, num!)
DECLARE SUB inpostxt (xptl, yptl, file$) 
DECLARE SUB posprn (xptl, yptl, txt$) 
DECLARE SUB posprncl (xpt!, ypt!, txt$, c!)
DECLARE SUB optprop (i, chl, glb, mss, oss, wvl(), wabs(), wsct(), phab(), spbc(), spbm(),
spbo(), gibcn, mssval, msscon, mssexp, ossval, osscon, ossexp, chirad, cmass, mmass,
mssrad, mssdens, omass, ossrad, ossdens, cbrat, mbrat, obrat, muO, a(), 
b(), att(), Kd(), Ref(), reftyp, parktot, parrtot)
```
DECLARE SUB bksct (b!(), bw, wvl!(), bksc!(), bchl!, bmss, boss, i!) DECLARE SUB modinp () DECLARE SUB printout (nw!, mss!, oss, ch!!, glb!, wvl(), a!(), b!(), att(), Kd!(), Ref!(), park, parr) DECLARE SUB printall (nw!, mss!, oss, ch!!, glb!, wv!!(), a!(), b!(), att!(), Kd!(), Ref!(), park, parr) DECLARE SUB filetitl (head\$, outpt\$) DECLARE SUB printfil () DECLARE SUB axes (x0!, xh!, y0!, yh!) DECLARE SUB label (x0!, xh!, y0!, yh!, yln!, xln!) DECLARE SUB conprn (mss!, oss, chi!, gib!) DECLARE SUB grplt (nw!, wvl!(), Ref!(), Kd!(), rupper!, kupper!, park, parr) DECLARE SUB filnum (filn!) DECLARE SUB pntfilx (out\$) DECLARE SUB pntoutn (nw!, mss!, oss, ch!!, glb!, wvl!(), a!(), b!(), att(), Kd!(), Ref!(), park, parr) DECLARE SUB filopen (fileout\$)

 $nw = 31: nlin = 32$

' instructions to restart or stop using F2 and F1 ***************************** ON KEY(1) GOSUB 200 $KEY(1) ON$ 10 ON KEY(2) GOSUB 10 KEY(2) ON

 $pi = 3.141593$

 $FOR x = 400 TO 700 STEP 10$ paren = $1/x +$ paren NEXT x f*x*4****4*#*w*ºAM! ***i**! t*44*fAi{*! f! **#*****ti**! **i4**i*i***ti#*4#t

' first screen - instructions to stop, option to change settings * '
20 Yurwi: Willinm We CLC 30 VIEW: WINDOW: CLS LINE (70,320)-(530,440), 15, B

DIM wvl(nw), wabs(nw), wsct(nw), phab(nw) DIM qsct(nw), mqsct(nw), spbc(nw), spbm(nw), oqsct(nw), spbo(nw) DIM SHARED a(nw), b(nw), bksc(nw), att(nw), Kd(nw), Ref(nw)

ON ERROR GOTO 555 SCREEN 12

CLS

calc level of PAR energy ***

```
posprn 25, 24, "Press F1 to QUIT at any time"
posprn 32, 25, "F2 to RESTART"
```

```
LINE (70, 20)-(530, 140), 15, B
LINE (72, 22)-(528, 138), 15, B
```
posprncl 16, 5, "Edit input file for equation constants (Y/N) ", 11

```
DO: ans$ = UCASE$(INKEY$)
LOOP UNTIL ans\hat{S} = "Y" OR ans\hat{S} = "N"
CLS.
IF ans\hat{S} = "Y" THEN modinp
IF ans \frac{1}{2} = "N" THEN eqfile \frac{1}{2} = "andinpos:dat" ELSE eqfile \frac{1}{2} = "colinpos.dat"
```
'input equation constants $***$ 45 OPEN eqfile\$ FOR INPUT AS #1 INPUT #1, watfl\$, chifl\$ INPUT #1, glbcn, mssval, msscon, mssexp, ossval, osscon, ossexp INPUT #1, chirad, chidens, chiref, mssrad, mssdens, mssref, ossrad, ossdens, ossref INPUT #1, cbrat, mbrat, obrat INPUT $#1$, reftyp, muO INPUT #1, rupper, kupper CLOSE #1

' Mie scat for chl: calc number of partls in conc **************************** 49 cmass = $4/3$ * pi * (chlrad * .000001) ^ 3 * chldens * 1E+09

```
mmass = 4/3 * pi * (mssrad * .000001) ^ 3 * mssdens * 1E+09
```

```
omass = 4/3 * pi * (ossrad * .000001) ^ 3 * ossdens * 1E+09
```

```
cnum = 40 / \text{cmass}mnum = 1000 / mmass
onum = 1000 / omass
```
55 OPEN watfl\$ FOR INPUT AS #201 OPEN chifls FOR INPUT AS #202

FOR $h = 1$ TO 2 LINE INPUT #201, head\$ LINE INPUT #202, head2\$ NEXT h

```
95 FORi = 1 TO rowINPUT #201, wvl(i), wabs(i), wsct(i)
 INPUT #202, wv, phab(i)
```
croe = 4 * pi * (chirad * .000001) / (wv * 1E-09) * chiref $mroe = 4 * pi * (mssrad * .000001) / (wv * 1E-09) * mssret$ oroe = $4 * pi * (ossrad * .000001) / (wv * 1E-09) * osset$ $qset(i) = 2 - (4 / \text{core} * \text{SIN}(\text{core})) + (4 / \text{core} * 2) * (1 - \text{COS}(\text{core}))$ masct(i) = $2 - (4 / m$ roe * SIN(mroe)) + $(4 / m$ roe \degree 2) * $(1 - COS(mroe))$ o qsct(i) = 2 - (4 / oroe * SIN(oroe)) + (4 / oroe ^ 2) * (1 - COS(oroe))

```
spbc(i) = pi / 4 * qsct(i) * cnum * ((chirad * 2 * .000001) ^ 2)
spbm(i) = pi / 4 * mqsct(i) * mnum * ((mssrad * 2 * .000001) ^ 2)
spbo(i) = pi / 4 * oqsct(i) * onum * ((ossrad * 2 * .000001) * 2)
```
NEXT i

```
CLOSE #201: CLOSE #202
```

```
'menu screen***
60 VIEW: WINDOW
CLS
LINE (30, 20)-(600, 350), 15, B
LINE (32, 22)-(598, 348), 15, B
```
posprn 18, 7, "Choose method to control concentration values"

```
posprn 12, 10, "1 - Alter values by increase/decrease keys and watch change "
posprn 12, 12, "2 - input exact values for each constituent"
posprn 12, 14, " 3 - Read all concentrations from a file "
```

```
posprn 25, 17, "[Press F1 to QUIT at any time]"
posprn 32, 18, "[F2 to RESTART]"
```

```
DO: menan$ = INKEY$
LOOP UNTIL menan\phi = "1" OR menan\phi = "2" OR menan\phi = "3"
```

```
IF menan\frac{1}{2} = "1" GOTO 250
IF menan\frac{1}{2} = "2" GOTO 350
IF menan\frac{1}{5} = "3" GOTO 450
```
' calculate reflectance *** 'option 1: increase/decrease concentrations ********************************* 250 VIEW: WINDOW

```
CLS
LINE (20, 10)-(580, 85), 15, B
LINE (20, 87)-(580, 87), 15
cch\ = "S"
posprn 6, 1, " Constituent concentrations "
posprn 15, 3, " MSS, mg/\vert OSS, mg/\vert Chi, mg/m3 g440, /m "
conprn mss, oss, chi, gib
posprn 4, 2, " To change, press M for MSS, O for OSS, C for Chl and G for Gelbstoff"
posprn 5, 5, " + \prime- increase/decrease TAB,/ multiply, divide increment by 10"
posprn 5, 6, " ESC to stop "
posprn 21, 6, " R to return to menu "
posprn 45, 6, " Z to set all conc to zero "
xpt = 24: ypt = 4: value = mss
IF echS = "S" THEN GOTO 275
```

```
DO: sign $ = INKEY$IF sign$ = CHR$(43) OR sign$ = CHR$(45) GOTO 516incch$ = UCASE$(sign$)
 IF incch\hat{S} = "R" GOTO 60
 IF incch\phi = "M" THEN cch\phi = "M"
 IF incch\hat{S} = "O" THEN cch\hat{S} = "O"IF incch$ = "C" THEN cch$ = "C"
 IF incch$ = "G" THEN cch$ = "G"
 IF incch$ = "Z" THEN cch$ = "Z"
```
LOOP UNTIL incch $\phi = "M"$ OR incch $\phi = "O"$ OR incch $\phi = "C"$ OR incch $\phi = "G"$ OR incch ϕ $=$ "Z"

```
IF CCNS = "M" THEN XPI = 18: YPI = 4: INC = .5: Value = mss<br>IF cchS = "O" THEN xnt = 31: ynt = 4: inc = 5: value = oss
IF cch$ = "0" THEN xpt = 31: ypt = 4: inc = . 
5: value = oss 
IF cch$ = "C" THEN xpt = 45: ypt = 4: inc = . 
5: value = chi 
IF cch$ = "G" THEN xpt = 58: ypt = 4: inc = . 
05: value = glb 
IF \text{cch}$ = "Z" THEN
 mss = 0: \text{oss} = 0: chl = 0: glb = 0
 conprn mss, oss, chi, gib 
 cch$ = "S"
 GOTO 275 
END IF
```

```
505 DO: posprn xpt, ypt, STR$(value) 
 sign$ = INKEY$LOOP UNTIL SIGN$ = CHR$(43) OR sign$ = CHR$(45) OR sign$ = CHR$(27) OR sign$ =<br>CUPA'O\ OR sin=A = CUPA'47\
CHR<sup>2</sup>(9) OR sign<sup>2</sup> = CHR<sup>2</sup>(47)IF sign$ = CHR$(9) THEN
 inc = inc * 10
 GOTO 505 
END IF 
IF sign$ = CHR$(47) THEN
 inc = inc / 10GOTO 505 
END IF 
IF sign\phi = CHR$(27) GOTO 500
515 DO 
 sign2\ = INKEY$
 IF sign2$ = CHR$(27) OR sign2$ = CHR$(9) OR sign2$ = CHR$(47) OR sign2$ =
CHR<sup>6</sup>(43) OR sign2<sup>6</sup> = CHR<sup>6</sup>(45) GOTO 520
```

```
516 IF sign$ = CHR$(43) THEN
  value = value + inc
 END IF 
 IF sign$ = CHR$(45) THEN
                   inc 
   value = value -<br>No ic
 END IF 
IF value \leq 0 THEN value = 0
 posprn xpt, ypt, STR$(value) +"" 
                                       n
IF cch$ = "M" THEN mss = value
 IF cch\phi = "O" THEN oss = value
 IF cch$ = "C" THEN chi = value
IF cch$ = "G" THEN glb = value
```
275 \sim 'calculation of a, b, K and R ************** $FOR i = 1 TO nw$ optprop i, chl, glb, mss, oss, wvl(), wabs(), wsct(), phab(), spbc(), spbm(), spbo(), glbcn,

```
mssval, msscon, mssexp, ossval, osscon, ossexp, chirad, cmass, mmass, mssrad, mssdens, 
omass, ossrad, ossdens, cbrat, mbrat, obrat, muO, a(), b(), att(),
Kd(), Ref(), reftyp, parktot, parrtot
NEXT i 
park = parktot / paren: parktot = 0
```

```
part = parrtot / paren: parrtot = 0
```

```
grplt nw, wvl(), Ref(), Kd(), rupper, kupper, park, parr
```

```
SLEEP 1
```
IF $ech\$ = "S" THEN GOTO 270

510 LOOP

500 **GOTO 270**

' option 2: input exact concentrations ********************* 350 pntfilx out\$

VIEW: WINDOW CLS LINE (20, 10)-(580, 85), 15, B LINE (20, 87)-(580, 87), 15

 cch \$ = " l "

```
posprn 6, 1, " Constituent concentrations "
posprn 15, 3, " MSS, mg/l OSS, mg/l Chl, mg/m3 g440, /m "
```
LOCATE 4, 18: INPUT mss LOCATE 4, 31: INPUT oss LOCATE 4, 45: INPUT chl LOCATE 4, 58: INPUT glb

posprn 4, 5, " To change, press M for MSS, O for OSS, C for Chi and G for Gelbstoff" posprn 20, 6, " R to return to menu, P to print to file "

370 FOR $i = 1$ TO nw

optprop i, chl, glb, mss, oss, wvl(), wabs(), wsct(), phab(), spbc(), spbm(), spbo(), glbcn, mssval, msscon, mssexp, ossval, osscon, ossexp, chirad, cmass, mmass, mssrad, mssdens, omass, ossrad, ossdens, cbrat, mbrat, obrat, muO, a(), b(), att() _

```
, Kd(), Ref(), reftyp, parktot, parrtot
 NEXT i
 park = parktot / parent: parktot = 0parr = parrtot / paren: parrtot = 0posprn 9, 7, "
grplt nw, wvl(), Ref(), Kd(), rupper, kupper, park, parr
```

```
375 DO: cch$ = UCASE$(INKEY$)
LOOP UNTIL cch$ = "M" OR cch$ = "O" OR cch$ = "C" OR cch$ = "G" OR cch$ = "R" OR
ech\ = "P"
```
w

```
IF cch$ = "P" THEN
 posprn 9, 7, "\mathbf{H}COLOR 12: LOCATE 7, 10: INPUT "Filename: ", fileout$: COLOR 15
 filopen fileout$
pntoutn nw, mss, oss, chl, glb, wvl(), a(), b(), att(), Kd(), Ref(), park, parr
```
CLOSE #31: CLOSE #32: CLOSE #33: CLOSE #34: CLOSE #35 **GOTO 375**

END IF

```
IF cch\ = "M" THEN
 posprn 18, 4, "
 LOCATE 4, 18: INPUT mss
ELSEIF \cosh s = "O" THEN
 posprn 31, 4, "LOCATE 4, 31: INPUT oss
ELSEIF \cosh s = "C" THEN
 posprn 45, 4, "
 LOCATE 4, 45: INPUT chi
ELSEIF \text{cch}$ = "G" THEN
 posprn 58, 4, "
 LOCATE 4, 58: INPUT glb
ELSEIF \cosh s = "R" THEN GOTO 60
END IF
```
GOTO 370

```
'option 3: input values from a file ******450 VIEW: WINDOW
CLS
LINE (30, 20)-(600, 350), 15, B
LINE (32, 22)-(598, 348), 15, B
posprn 35, 5, "INPUT FILE "
posprn 7, 8, " The ASCII file should have one header line for general comments, "
posprn 11, 9, " followed by the number of sites/samples on the next line. "
posprn 9, 11, " The successive lines should each represent one site/sample"
posprn 32, 12, " in the form "
posprn 24, 13, " mss oss chi glb "
posprn 23, 14, " with spaces between each value "
```
LOCATE 16, 28: INPUT " Input file: ", infile\$

```
455 OPEN infiles FOR INPUT AS #31
LINE INPUT #31, head$
INPUT #31, nst
```

```
posprncl 23, 18, " Output values to a file (Y/N): ", 11
```

```
DO: out$ = UCASE$(INKEY$)LOOP UNTIL out$ = "Y" OR out$ = "N"
```

```
posprn 20, 18, "
```
 \mathbf{u}

```
IF out \phi = "Y" THEN
printfil
```

```
DO: output$ = UCASE$(INKEY$)
LOOP UNTIL outpt$ = "T" OR outpt$ = "A"
END IF
```

```
458
```
posprn 28, 18, " Number of stations: " + STR\$(nst)

```
posprncl 18, 20, " Move through automatically or manually (A/M): ", 11
DO: page $ = UCASE$(INKEY$)LOOP UNTIL page$ = "A" OR page$ = "M"
```
LINE (30, 390)-(600, 410), 15, B posprn 6, 25, " Press ESC to continue " DO: LOOP UNTIL INKEY\$ = CHR\$(27)

IF out $\phi = "Y"$ THEN filetitl heads, outpts

```
CLS 
LINE (20,10)-(580,85), 15, B 
LINE (20,87)-(580,87), 15
```

```
posprn 6, 1, " Constituent concentrations "
posprn 17,3, " MSS, mg/I OSS, mg/I Chi, mg/m3 g440, /m " 
IF page$ = "M" THEN posprn 27, 5, " Press ESC to continue "
posprn 25, 6, " R to return to input menu "
posprn 4, 2, " Input file: " + infile $
posprn 60, 2, " total: " + STR$(nst)
posprn 35, 2, "row of data: "
```

```
460 FOR s = 1 TO nst
 INPUT #31, mss, oss, chi, gib 
 IF mss < 0 THEN mss = 0
 conprn mss, oss, chi, gib 
 posprn 47, 2, STR$s() + "
```

```
FOR i = 1 TO nw
```
optprop i, chi, gib, mss, oss, wvl(), wabs(), wsct(), phab(), spbc(), spbm(), spbo(), glbcn, mssval, msscon, mssexp, ossval, osscon, ossexp, chlrad, cmass, mmass, mssrad, mssdens, omass, ossrad, ossdens, cbrat, mbrat, obrat, mu0, a(), b(), att() , Kd(), Ref(), reftyp, parktot, parrtot NEXT i

```
park = parktot / paren: parktot = 0
parr = parrtot / paren: parrtot = 0
```
grplt nw, wvl(), Ref(), Kd(), rupper, kupper, park, parr

```
IF out \phi = "Y" AND outpt \phi = "T" THEN printout nw, mss, oss, chl, glb, wvl(), a(), b(), att(),
Kd(), Ref(), park, parr 
 IF out \phi = "Y" AND outpt \phi = "A" THEN printall nw, mss, oss, chi, gib, wvi(), a(), b(), att(),
Kd(), Ref(), park, parr
```

```
IF page$ = "M" THEN
  DO: cont$ = UCASE$(INKEY$)LOOP UNTIL cont\phi = \text{CHR}\(27) OR cont\phi = "R"H conts = "R" THEN GOTO 470
 END IF 
 IF page$ = "A" THEN IF UCASE$(INKEY$) = "R" THEN GOTO 470
NEXT s
```

```
IF page$ = "A" THEN DO: LOOP UNTIL UCASE$(INKEY$) = "R"
470 CLOSE #31: CLOSE #101: CLOSE #102: CLOSE #103: CLOSE #104: CLOSE #105 
GOTO 60
```

```
520 SELECT CASE sign2$
CASE IS = CHR<sup>2</sup>(27)GOTO 500
CASE IS = CHR<sup>3</sup>(9)inc = inc * 10GOTO 510
CASE IS = CHR<sup>3</sup>(47)inc = inc / 10GOTO 510
CASE IS = CHR$(43)
sign\ = CHR$(43)
GOTO 510
CASE IS = CHR$(45)
sign$ = CHR$(45)
GOTO 510
```

```
END SELECT
```

```
"identify and print type of error **************************
555
VIEW: WINDOW
posprn 45, 28, " Error: " + STR$(ERR) + " on line " + STR$(ERL) + " "
SELECT CASE ERR
CASE IS = 53LOCATE 18, 15: INPUT " File not found, please try again: ", infile$
posprn 15, 18, "
RESUME 455
END SELECT
STOP
```

```
200 VIEW: WINDOW
CLS
LINE (60, 140)-(540, 194), 15, B
LINE (58, 138)-(542, 196), 15, B
```

```
posprn 30, 11, "THAT'S ALL FOLKS!! "
END
```

```
SUB axes (x0, xh, y0, yh)
' plot axes of graphs ******
```

```
xint = (xh - x0) / 6; yien = xint / 5
yint = (yh - y0) / 5: xlen = yint / 20
```

```
FOR xln = x0 TO xh STEP xintLINE (x \ln y0 + x \ln^{-1}(x \ln y0))NEXT xln
```
FOR $yln = y0$ TO yh STEP $yint$ LINE $(x0, yin)$ - $(x0 - ylen, yin)$ NEXT yin

END SUB

SUB bksct (b(), bw, wvl(), bksc(), bchl, bmss, boss, i)

 $bconst = .019$ $bcons = bconst$

'Gordon et al, 1988 to allow for wavelength dependency below 0.1 mg/m3 'IF chl \leq .1 THEN "bcons = $(560 / \text{wvl}(i))$ * .019 'END IF

```
* * * * * * * * * * * * * * * * * * *
' chl bkscatter Morel&Bricaud 1981
bbch1 = bch1 * .002
bbmss = bmss * .019
bboss = boss *.01
```

```
bksc(i) = bbchl + bbmss + bboss + bw *.5
```
END SUB

SUB conprn (mss, oss, chl, glb)

'print values of concentrations

```
posprn 18, 4, STR<sup>3</sup>(ms) + "posprn 31, 4, STR$(\cos) + "
posprn 45, 4, STR$(chl) + "
posprn 58, 4, STR$(glb) + "\bullet\bullet
```
END SUB

SUB filetitl (head\$, outpt\$)

' print title in output files ****

PRINT #101, " ABS "; head\$ PRINT #102, " SCT "; head\$ PRINT #103, " ATT "; head\$ PRINT #104, " REF "; head\$

IF outpt $\phi = "T"$ THEN PRINT #101, " mss **OSS** chl glb 700 " PRINT #102, " mss chl **OSS** glb 700 " PRINT #103, " mss chl glb **OSS** 700 PAR " PRINT #104, " mss oss chi glb PAR "

ELSE

PRINT #101,

" mss glb **OSS** – chl 700 " **PRINT #102,** \mathbf{H} chi d gib mss **OSS** 700 "

PRINT #103,

 $\mathbf{H}_{\mathcal{A}}$ 400 410 420 430 440 450 glb 460 480 chl. mss **OSS** 470 490 510 520 530 540 550 560 570 590 500 580 600 620 630 610 660 680 640 650 670 690 700 PAR "

PRINT #104,

400 410 420 \mathbf{u} glb 430 440 450 460 470 480 mss chl **OSS** 490 520 510 530 540 550 560 570 580 590 600 620 630 500 610 650 660 670 680 690 PAR " 700 640

 \bullet

END IF

END SUB

SUB filopen (fileout\$) * * * * * * * * * *

```
' open files for option 2 ****************
```

```
31 OPEN fileout$ + ".abs" FOR OUTPUT AS #31
32 OPEN fileout$ + ".sct" FOR OUTPUT AS #32
33 OPEN fileout$ + ".att" FOR OUTPUT AS #33
34 OPEN fileout$ + ".ref" FOR OUTPUT AS #34
35 OPEN fileout$ + ".bma" FOR OUTPUT AS #35
```
END SUB

```
SUB grplt (nw, wvl(), Ref(), Kd(), rupper, kupper, park, parr)
'plot graphs of attenuation and reflectance ***********************************
form$ = "& \##.##"
```

```
posprn 55, 8, "REFLECTANCE"
posprn 47, 18, " DIFFUSE ATTENUATION "
```

```
VIEW (75, 127)-(525, 267), , 15
```

```
WINDOW (400, rupper)-(700, 0)
CLS 1
axes 400, 700, 0, rupper
label 400, 700, 0, rupper, 5, 18
LOCATE 10, 50: PRINT ; USING form$; "PAR R = "; parr
```
 $FOR i = 1 TO nw$ IF wvI(i) $>$ 400 THEN LINE (wvl(i), Ref(i))-(wvl(i - 1), Ref(i - 1)), 15 END IF NEXT i

VIEW: WINDOW

280 VIEW (75, 289)-(525, 429), , 15 WINDOW (400, kupper)-(700, 0) CLS 1

```
axes 400, 700, 0, kupper
label 400, 700, 0, kupper, 5, 28
```

```
LOCATE 20, 50: PRINT ; USING form$; "PAR K ="; park
FOR i = 1 TO nwIF wyl(i) > 400 THEN
  LINE (wvI(i), Kd(i))-(wvI(i - 1), Kd(i - 1)), 15
 END IF
NEXT i
END SUB
```

```
SUB inposprn (xpt, ypt, txt$, num)
'input values, showing defaults **********
```

```
whitxt$ = txt$ + STR$(num) + "): "
```

```
LOCATE ypt, xpt
PRINT whitxt$;
INPUT inp$
```

```
IF inp$ = "" THEN
 num = numELSE
 num = VAL(inp<sup>§</sup>)END IF
```
END SUB

SUB inpostxt (xpt, ypt, file \$) ' input text, showing defaults **

 \bullet

```
whitxt$ = "(" + file$ + "): "
LOCATE ypt, xpt
PRINT whitxt$;
INPUT inp$
IF inp$ = "" THEN
 file \frac{1}{2} = file $
ELSE
  file \hat{\mathsf{s}} = \mathsf{inp}\, \hat{\mathsf{s}}END IF
```
END SUB

SUB label (x0, xh, y0, yh, yin, xln) 'label graph axes ****

```
IF xln = 18 GOTO 600
posprn yin + 2, xin, STR$(x0)
posprn yln + 60, xln, STR$(xh)600
posprn yln, xln - 9, STR$(yh)
posprn yin, xin - 1, STR$(y0)
```
END SUB

SUB modinp

' input default values from file

OPEN "andinpos.dat" FOR INPUT AS #1 INPUT #1, watfl\$ INPUT #1, chifi\$ INPUT #1, glbcn, mssval, msscon, mssexp, ossval, osscon, ossexp INPUT #1, chirad, chidens, chiref, mssrad, mssdens, mssref, ossrad, ossdens, ossref INPUT #1, cbrat, mbrat, obrat INPUT #1, reftyp, muO INPUT #1, rupper, kupper CLOSE #1

```
posprn 65,3, "1 out of 3" 
posprn 4, 4, "ABSORPTION"
posprn 5,6, "Input files at 10 nm intervals 400-700nm" 
posprn 6,8, "water has 2 header lines, " 
posprn 7,9, "then wvl, abs and scat on each line" 
posprn 6,11, "chlorophyll file has 2 header lines, " 
posprn 7,12, "then wvl and specific abs on each line"
```

```
posprn 50,8, "water file" 
inpostxt 51,9, watfl$ 
posprn 50,11, "chlorophyll file" 
inpostxt 51, 12, chifi$
```

```
inposprn 55,15, "m (", glbcn 
inposprn 55, 18, "1 (", massval)inposprn 55, 19, "p (", msscon)inposprn 55, 20, "n (", mssexp)inposprn 55,22, "j (", ossval 
inposprn 55,23, "I (", osscon 
inposprn 55, 24, "h (", ossexp")
```

```
posprn 5,14, "Gelbstoff equation" 
posprn 6, 15, "a = g440 e xp(m * (wvl-440))"
posprn 5,18, "Mineral suspended solids" 
posprn 6, 19, "a = 1*MSS + p*MSS*exp(n * (wvl-440))"
posprn 5,22, "Other suspended solids"
```

```
posprn 6, 23, "a = j*OSS + k*OSS*exp(h * (wvl-440))"
```

```
LINE (380,20)-(620,425), 15, B 
posprn 50,5, "Default values in brackets" 
posprn 51,6, "Press RETURN if correct"
```

```
posprn 4,4, "SCATTERING" 
posprn 5,8, "Chlorophyll based on Mie: ref index cm" 
posprn 6, 9, "radius x "
posprn 6,10, "density y (1.03-1.10 g/cm3)" 
posprn 5,11, "backscattering ratio bbc " 
posprn 5,14, "Mineral suspended solids: ref index mm" 
posprn 6,15, "radius w" 
posprn 6,16, "density z" 
posprn 5, 17, "backscattering ratio bbm "
posprn 5,20, "Other suspended solids: ref index om" 
posprn 6, 21, "radius v "
posprn 6,22, "density u" 
posprn 5, 23, "backscattering ratio bbo "
```
50

```
LINE (15,440)-(620,460), 15, B
```

```
posprncl 6,28, " Are all values correct? (Y/N) ", 11
```

```
DO: ans$ = UCASE$(INKEY$)LOOP UNTIL ans\hat{S} = "Y" OR ans\hat{S} = "N"IF ans\delta = "N" GOTO 50
```
'********N***iii********************** ** ** IF ***. ***N*****i ** **** il' **. *****

 \mathcal{L}

```
CLS 
LINE (15,20)-(360,425), 15, B
```

```
LINE (380, 20)-(620, 425), 15, B
posprn 50, 5, "Default values in brackets"
posprn 51, 6, "Press RETURN if correct"
posprn 65, 3, "2 out of 3"
```

```
70 inposprn 55, 8, " cm (", chiref
inposprn 55, 9, "\times (", chirad
inposprn 55, 10, "y (", chidens
inposprn 55, 11, " bbc (", cbrat
inposprn 55, 14, " mm (", mssref
inposprn 55, 15, " w (", mssrad
inposprn 55, 16, " z (", mssdens
inposprn 55, 17, " bbm (", mbrat
inposprn 55, 20, " om (", ossref
inposprn 55, 21, "v (", ossrad")
```

```
inposprn 55, 22, " u (", ossdens
inposprn 55, 23, " bbo (", obrat
```
LINE (15, 440)-(620, 460), 15, B

```
posprncl 6, 28, " Are all values correct? (Y/N) ", 11
```

```
DO: ans$ = UCASE$(INKEY$)LOOP UNTIL ans \hat{s} = "Y" OR ans \hat{s} = "N"
IF ans \phi = "N" GOTO 70
\blacksquare***
```
CLS LINE (15, 20)-(620, 400), 15, B

```
posprn 65, 3, "3 out of 3"
```

```
posprn 8, 4, "Calculation of Kd and R using Kirk's algorithms:"
posprn 11, 6, "DIFFUSE ATTENUATION"
posprn 12, 7, " Kd = (a/mu0) * (1 + 0.256 * b/a)^{\circ}0.5 "
```

```
posprn 11, 10, "REFLECTANCE"
posprn 12, 11, "1. R = 0.33 * bb/a "
posprn 12, 12, "2. R = (0.975 \cdot 0.629 \text{ mu0}) * b b/a"
80 inposprn 11, 13, "Reflectance equation (", reftyp
```

```
inposprn 21, 16, "mu0 (", mu0
posprn 12, 19, "Upper values for y-axes on graphs (lower is zero) "
inposprn 23, 20, " R (", rupper
inposprn 23, 21, "K', kupper
```

```
LINE (15, 440)-(620, 460), 15, B
```

```
posprncl 6, 28, " Are all values correct? (Y/N) ", 11
```

```
DO: ans$ = UCASE$(INKEY$)LOOP UNTIL ans\hat{\phi} = "Y" OR ans\hat{\phi} = "N"
IF ans\hat{S} = "N" GOTO 80
```
OPEN "colinpos.dat" FOR OUTPUT AS #11 PRINT #11, watfl\$ PRINT #11, chifi\$ PRINT #11, glbcn PRINT #11, mssval PRINT #11, msscon PRINT #11, mssexp PRINT #11, ossval PRINT #11, osscon PRINT #11, ossexp PRINT #11, chirad PRINT #11, chidens PRINT #11, chiref PRINT #11, mssrad PRINT #11, mssdens PRINT #11, mssref PRINT #11, ossrad PRINT #11, ossdens PRINT #11, ossref PRINT #11, cbrat PRINT #11, mbrat PRINT #11, obrat PRINT #11, reftyp PRINT #11, mu0 PRINT #11, rupper PRINT #11, kupper **CLOSE #11**

END SUB

SUB optprop (i, chl, glb, mss, oss, wvl(), wabs(), wsct(), phab(), spbc(), spbm(), spbo(), glbcn, mssval, msscon, mssexp, ossval, osscon, ossexp, chirad, cmass, mmass, mssrad, mssdens, omass, ossrad, ossdens, cbrat, mbrat, obrat, muO, a(), b(),

att(), Kd(), Ref(), reftyp, parktot, parrtot) ' calculate absorption, scattering, attenuation and reflectance *************

```
achI = phab(i) * chIag/b = g/b * EXP(glbcn * (wvl(i) - 440))amss = mssval * mss + msscon * mss * EXP(mssexp * (wvi(i) - 440))
omss = ossval * oss + osscon * oss * EXP(ossexp * (wvl(i) - 440))
a(i) = achl + aglb + amss + wabs(i)
```

```
bchl = spbc(i) * chlbmss = sbm(i) * mssboss = spbo(i) * oss
```

```
' IF wvl(i) > 600 THEN bmss = bmss * (600 / wvl(i)) ^ 2
 b(i) = bmss + bch! + bossbw = wsct(i)
```
'calculate attenuation

 $att(i) = b(i) + a(i)$

'calculate backscatter bksct b(), bw, wvl(), bksc(), bchl, bmss, boss, i

'reflectance coeffs [*100 to convert to percentages]:

IF reftyp = 2 THEN Ref(i) = $(0.975 - 0.629 * mu0) * b ksc(i) / a(i)) * 100$ IF reftyp = 1 THEN Ref(i) = .33 * bksc(i) / a(i) * 100

```
Kd(i) = (1 / mu0) * (1 + (.425 * mu0 - .19) * b(i) / a(i)) ^ .5 * a(i)
IF wyl(i) < 701 AND wyl(i) > 399 THEN
 parktot = parktot + Kd(i) * 1 / wvl(i)
 parrtot = parrtot + Ref(i) * 1 / wvl(i)
END IF
```
END SUB

```
SUB pntfilx (out$)
'option to print to file, and details, for option 3
```
VIEW: WINDOW CLS LINE (20, 20)-(580, 125), 15, B LINE (20, 127)-(580, 127), 15

```
filn = 1posprncl 7, 3, "Print to file (Y/N) ", 11
```

```
DO: out$ = UCASE$(INKEY$)LOOP UNTIL out$ = "Y" OR out$ = "N"
```

```
IF out \phi = "N" THEN GOTO 320
```
posprn 11, 5, " Type P when you wish to print the values to a file " posprn 8, 6, " There will be a prompt to enter the stem of the filename " posprn 6, 7, " The extensions .abs, .sct, .bma, .att and .ref will be added "

LINE (30, 390)-(600, 410), 15, B posprn 6, 25, " Press ESC to continue "

```
DO: LOOP UNTIL INKEY$ = CHR$(27)
```
SUB pntoutn (nw, mss, oss, chl, glb, wvl(), a(), b(), att(), Kd(), Ref(), park, parr) ' print option 2 files at 10 nm intervals **************

formd\$ = " ### ###.## "

PRINT #31, " MSS = "; mss, " OSS = "; oss, " ChI = "; chI, " $q440 =$ "; glb PRINT #32, " MSS = "; mss, " OSS = "; oss, " Chl = "; chl, " $q440 =$ "; glb PRINT #33, " MSS = "; mss, " OSS = "; oss, " Chi = "; chi, " $q440 =$ "; glb PRINT #34, " MSS = "; mss, " OSS = "; oss, " Chl = "; chl, " $q440 =$ "; glb PRINT #35, " MSS = "; mss, " OSS = "; oss, " Ch! = "; ch!, " g440 = "; glb

PRINT #33, " PAR $K =$ "; USING formd\$; park PRINT #34, " PAR R = "; USING formd\$; parr

 $FOR i = 1 TO nw$

```
PRINT #31, USING formd$; wvl(i); a(i)
 PRINT #32, USING formd$; wvl(i); b(i)
 PRINT #33, USING formd$; wvl(i); Kd(i)
 PRINT #34, USING formd$; wvl(i); Ref(i)
 PRINT #35, USING formd$; wvl(i); att(i)
NEXT i
```
END SUB

```
SUB posprn (xpt, ypt, txt$)
```
' print text

LOCATE ypt, xpt PRINT txt\$

END SUB

```
SUB posprncl (xpt, ypt, txt$, c)
" print coloured text **
```
COLOR_c LOCATE ypt, xpt PRINT txt\$ COLOR 15

END SUB

 $\ddot{}$

SUB printall (nw, mss, oss, chl, glb, wvl(), a(), b(), att(), Kd(), Ref(), park, parr) ' print option 3 files at 10 nm intervals $***********$

```
formc$ = " ###.## ##.## ##.## "
forms$ = " \# \# \# "
```
PRINT #101, USING forme\$; mss; oss; chl; glb; PRINT #102, USING formc\$; mss; oss; chl; glb; PRINT #103, USING formc\$; mss; oss; chl; glb; PRINT #104, USING formc\$; mss; oss; chl; glb; PRINT #105, USING forme\$; mss; oss; chl; glb;

 $FOR i = 1 TO nw$ PRINT #101, USING forms\$; a(i); PRINT #102, USING forms\$; b(i);

PRINT #103, USING forms\$; Kd(i); PRINT #104, USING forms\$; Ref(i); PRINT #105, USING forms\$; att(i); NEXT i

PRINT #101, : PRINT #102, : PRINT #103, park: PRINT #104, parr: PRINT #105, **END SUB**

SUB printfil CLS 2

LINE (30, 20)-(600, 350), 15, B LINE (32, 22)-(598, 348), 15, B

posprn 15, 7, " Four files will be made with the trunk: colout " posprn 17, 8, " and the extensions: .abs, .sct, .att, .ref " posprn 23, 10, " The concentrations will be printed "

```
posprn 14, 11, " and then the optical properties at 10 wavelengths (T): "
posprn 15, 13, "410 440 490 510 520 550 570 600 670 700 "
posprn 23, 15, " or at 10 nm intervals (A)"
posprncl 55, 15, "T or A: ", 11
```
OPEN "colout.abs" FOR OUTPUT AS #101 OPEN "colout.sct" FOR OUTPUT AS #102 OPEN "colout.att" FOR OUTPUT AS #103 OPEN "colout.ref" FOR OUTPUT AS #104 OPEN "colout.bma" FOR OUTPUT AS #105

END SUB

SUB printout (nw, mss, oss, chl, glb, wvl(), a(), b(), att(), Kd(), Ref(), park, parr)
'print option 3 files at 10 wavelengths ***********************************

```
formc$ = " # # # # # # # # # # # # # # "forms$ = "###.##"
```
PRINT #101, USING formc\$; mss; oss; chi; glb; PRINT #102, USING formc\$, mss; oss; chi; gib; PRINT #103, USING formc\$; mss; oss; chi; glb; PRINT #104, USING formc\$; mss; oss; chi; gib; PRINT #105, USING formc\$; mss; oss; chi; gib;

 $FOR i = 1 TO nw$ IF wvl(i) $=$ 410 THEN PRINT #101, USING forms\$; a(i); PRINT #102, USING forms\$; b(i); PRINT #103, USING forms\$; Kd(i); PRINT #104, USING forms\$; Ref(i); PRINT #105, USING forms\$; att(i); END IF

```
IF wvi(i) = 440 THEN
 PRINT #101, USING forms$; a(i); 
 PRINT #102, USING forms$; b(i); 
 PRINT #103, USING forms$; Kd(i); 
 PRINT #104, USING forms$; Ref(i); 
 PRINT #105, USING forms$; att(i); 
END IF
```

```
IF wvl(i) = 490 THEN
 PRINT #101, USING forms$; a(i); 
 PRINT #102, USING forms$; b(i); 
 PRINT #103, USING forms$; Kd(i); 
 PRINT #104, USING forms$; Ref(i); 
 PRINT #105, USING forms$; att(i); 
END IF
```

```
IF wvillet = 510 THEN
 PRINT #101, USING forms$; a(i); 
 PRINT #102, USING forms$; b(i);
 PRINT #103, USING forms$; Kdii); 
 PRINT #104, USING forms$; Ref(i); 
 PRINT #105, USING forms$, att(i); 
END IF
```

```
IF wvi(i) = 520 THEN
 PRINT #101, USING forms$; a(i);
```
IF wvI (i) = 550 THEN PRINT #101, USING forms\$; a(i); PRINT #102, USING forms\$; b(i); PRINT #103, USING forms\$; Kd(i);

```
PRINT #102, USING forms$; b(i); 
 PRINT #103, USING forms$; Kd(i); 
 PRINT #104, USING forms$; Ref(i); 
 PRINT #105, USING forms$; att(i); 
END IF
```
PRINT #104, USING forms\$; Ref(i); PRINT #105, USING forms\$; att(i); END IF

IF wvl(i) $=$ 570 THEN PRINT #101, USING forms\$; a(i); PRINT #102, USING forms\$; b(i); PRINT #103, USING forms\$; Kd(i); PRINT #104, USING forms\$; Ref(i); PRINT #105, USING forms\$; att(i); END IF

IF wvl(i) $=$ 600 THEN PRINT #101, USING forms\$; a(i); PRINT #102, USING forms\$; b(i);

IF wvl(i) $= 670$ THEN PRINT #101, USING forms\$; a(i); PRINT #102, USING forms\$; b(i); PRINT #103, USING forms\$; Kd(i); PRINT #104, USING forms\$; Ref(i); PRINT #105, USING forms\$; att(i); END IF

IF wvl(i) $= 700$ THEN PRINT #101, USING forms\$; a(i) PRINT #102, USING forms\$; b(i) PRINT #103, USING forms\$; Kd(i); PRINT #104, USING forms\$; Ref(i);

```
PRINT #103, USING forms$; Kd(i); 
 PRINT #104, USING forms$; Ref(i); 
 PRINT #105, USING forms$; att(i); 
END IF
```
PRINT #103, USING forms\$; park PRINT #104, USING forms\$; parr

PRINT #105, USING forms\$; att(i) END IF NEXT i

END SUB

APPENDIX XI

Symbol Explanation

SYMBOLS

- a absorption coefficient
- a_c, a_p absorption due to chlorophyll and particles respectively a_d, a_m absorption due to detritus and minerals respectively
- absorption due to detritus and minerals respectively
- a_w, , absorption due to pure water and yellow substance respectivel
- a^{*} specific absorption
A_c constant of absorption A_c constant of absorption due to chlorophyll
b scattering coefficient
-
- b scattering coefficient
b_b backscatter coefficier b_{b} backscatter coefficient
 b_{b} backscatter ratio
	-
- b_b backscatter ratio
b_c,b_w scatter due to ch b_c, b_w scatter due to chlorophyll and pure water respectively B_c constant of scatter due to chlorophyll
- constant of scatter due to chlorophyll
- c beam attenuation coefficient
- $C \equiv$ chl chlorophyll concentration mgm⁻³
D diameter of particles
- D diameter of particles
E irradiance
- irradiance
- E_d , E_u downward and upward irradiance
 E_0 scalar irradiance
-
- E_0 scalar irradiance
F(d) particle size disti $F(d)$ particle size distribution function
g(z) attenuation weighting factor
- attenuation weighting factor
- g_{440} = A_y (440) absorption of yellow substance at 440 nm
	- radiant intensity
- I_T total scattered radiation
K beam attenuation coeffi
-
- K_d beam attenuation coefficient
 K_d diffuse attenuation coefficient
- K_d diffuse attenuation coefficient
 K_E vertical attenuation for net do K_E vertical attenuation for net downward irradiance E_d . $E_{\mathbf{u}}$
- K_f efficiency factor or effective area coefficient
- radiance L_{r} , L_{u} apparent and L_r , L_u apparent and upward radiance
 L_0 scalar radiance scalar radiance m complex refractive index n refractive index for purely scattering particles
N number of particles per unit volume N number of particles per unit volume
Q_c efficiency factor for attenuation due efficiency factor for attenuation due to chlorophyll r distance between radiance source and receiving point (m)
R reflectance $(\%)$ R reflectance (%)
SM suspended mine SM suspended minerals $(gm⁻³)$
V volume $(m⁻³)$ volume $(m⁻³)$ z. depth (m)
z. mid-point of euphotic zone Z_u mud-point of euphone zone $z_q(1\%)$ depth at which 99% of irradiance has been attenuated $z_q(1\%)$ z_{90} depth at which 90% of irradiance has been attenuated pathlength amplification factor β volume scattering function X wavelength (nm) μ average cosine
 θ , Φ zenith and azin θ , Φ zenith and azimuthal angles
 \sum total suspended solids conce
 ξ ratio expression total suspended solids concentration mgl-' ratio expression ω_0 solid angle
 ω_0 scattering a scattering albedo

ACRONYMS

- AMB95 August Menai Bridge 1995 (Pier Survey)
- CS Colour Sensor (UCW)
- CZCS Coastal Zone Colour Scanner
- IRM1 Irradiance Meter (UCW)
- JMB94 July Menai Bridge 1994 (Pier Survey)
- MSS Mineral Suspended Solids
- PAR Photosynthetically Active Radiation

 $\mathbf{r} \in \mathbb{R}^{n \times n}$, where $\mathbf{r} \in \mathbb{R}^{n \times n}$

 \mathcal{A}^{\pm}

 \mathbf{r}